



US005641428A

United States Patent [19][11] **Patent Number:** **5,641,428**

Wingen et al.

[45] **Date of Patent:** **Jun. 24, 1997**

[54] **USE OF OPTICALLY ACTIVE 1,3-DIOXOLANE-4-CARBOXYLATES AS DOPES IN LIQUID-CRYSTAL MIXTURES, LIQUID-CRYSTAL MIXTURES CONTAINING THESE COMPOUNDS, AND NOVEL OPTICALLY ACTIVE 1,3-DIOXOLANE-4-CARBOXYLATES**

FOREIGN PATENT DOCUMENTS

306195	3/1989	European Pat. Off.	252/299.61
3604898	8/1987	Germany	.	
3604899	8/1987	Germany	.	
3739588	7/1988	Germany	.	

[75] **Inventors:** **Rainer Wingen**, Hattersheim am Main; **Hans-Rolf Dübal**, Königstein/Taunus; **Claus Escher**, Mühlthal; **Wolfgang Hemmerling**, Sulzbach; **Ingrid Müller**, Hofheim am Taunus; **Dieter Ohlendorf**, Liederbach, all of Germany

OTHER PUBLICATIONS

Takenaka et al., *Mol. Cryst. Liq. Cryst.*, vol. 131, pp. 257-271 (1985).

CA 74:3148t(1971).

CA 84:163740q (1976).

Morrison and Boyd, *Organic Chemistry*, 4th Ed., pp. 786-787 (1983).

Chemical Abstracts, vol. 88, p. 566, No. 22089e (Jan. 1978).

Chemical Abstracts, vol. 88, p. 566, No. 22094c (Jan. 1978).

[73] **Assignee:** **Hoechst Aktiengesellschaft**, Frankfurt, Germany

[21] **Appl. No.:** **879,147**

[22] **Filed:** **Apr. 30, 1992**

Related U.S. Application Data

[63] Continuation of Ser. No. 494,909, Mar. 9, 1990, abandoned, which is a continuation of Ser. No. 181,925, Apr. 15, 1988, abandoned.

[30] Foreign Application Priority Data

Apr. 18, 1987 [DE] Germany 37 13 273.3

[51] **Int. Cl.⁶** **C09K 19/34**

[52] **U.S. Cl.** **252/299.61**

[58] **Field of Search** **252/299.61**

[56] References Cited

U.S. PATENT DOCUMENTS

4,336,183	6/1982	Nakahara et al.	524/95
4,873,019	10/1989	Krause et al.	252/299.61

Primary Examiner—Cynthia Harris Kelly

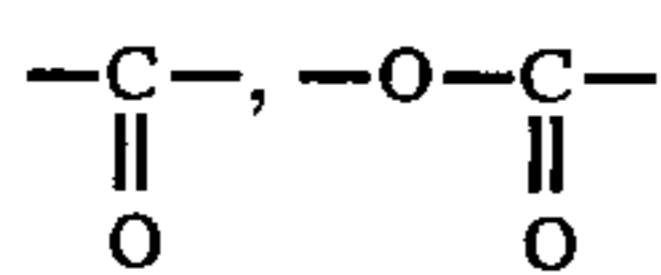
Attorney, Agent, or Firm—Curtis, Morris & Safford, PC

[57] ABSTRACT

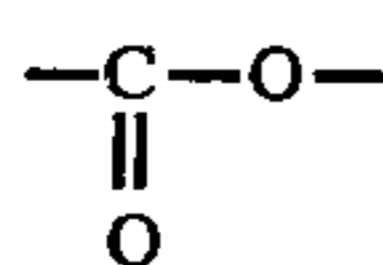
Optically active, mesogenic 1,3-dioxolane-4-carboxylates are suitable as dopes in liquid-crystal mixtures. They result in liquid-crystalline ferroelectric phases having short switching times and in electroclinic phases having large electroclinic coefficients. Their particular advantage is that they induce a helix of very large pitch, meaning that helix compensation by further dopes is unnecessary. In addition, the 1,3-dioxolane-4-carboxylates exhibit high UV stability.

6 Claims, No Drawings

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and/or



and for one or more H to be replaced by F, Cl, Br or CN, R² and R³ are each H or an alkyl radical having 1 to 10 carbon atoms, it being possible for one or more H to be replaced by F, or R² and R³, together with the C(2) atom of the dioxolane ring, form a cyclopentane, cyclohexane or cycloheptane ring,

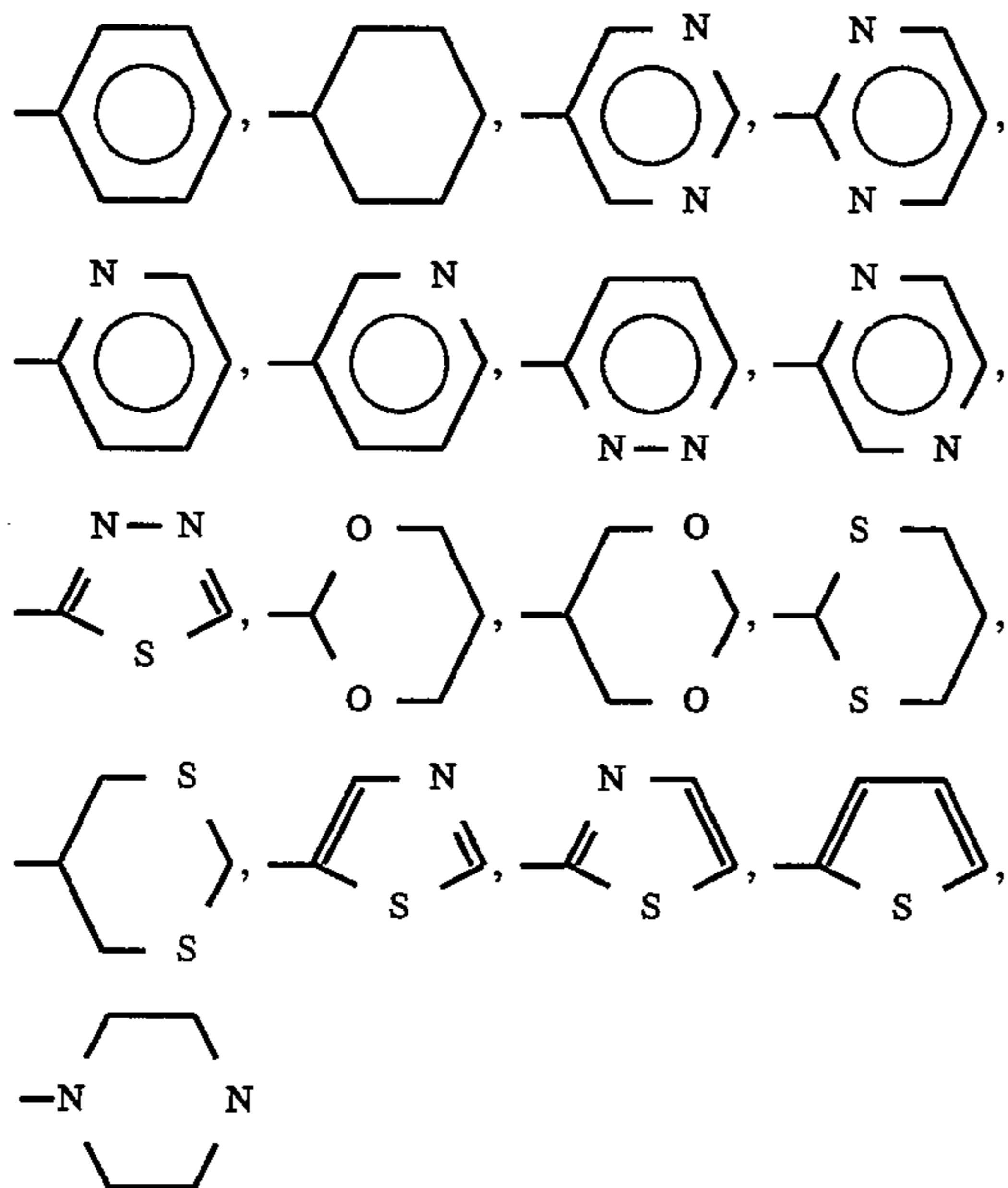
R⁴ denotes H or an alkyl radical having 1 to 10 carbon atoms or an alkenyl radical having 2 to 10 carbon atoms,

j and l denote zero, 1 or 2,

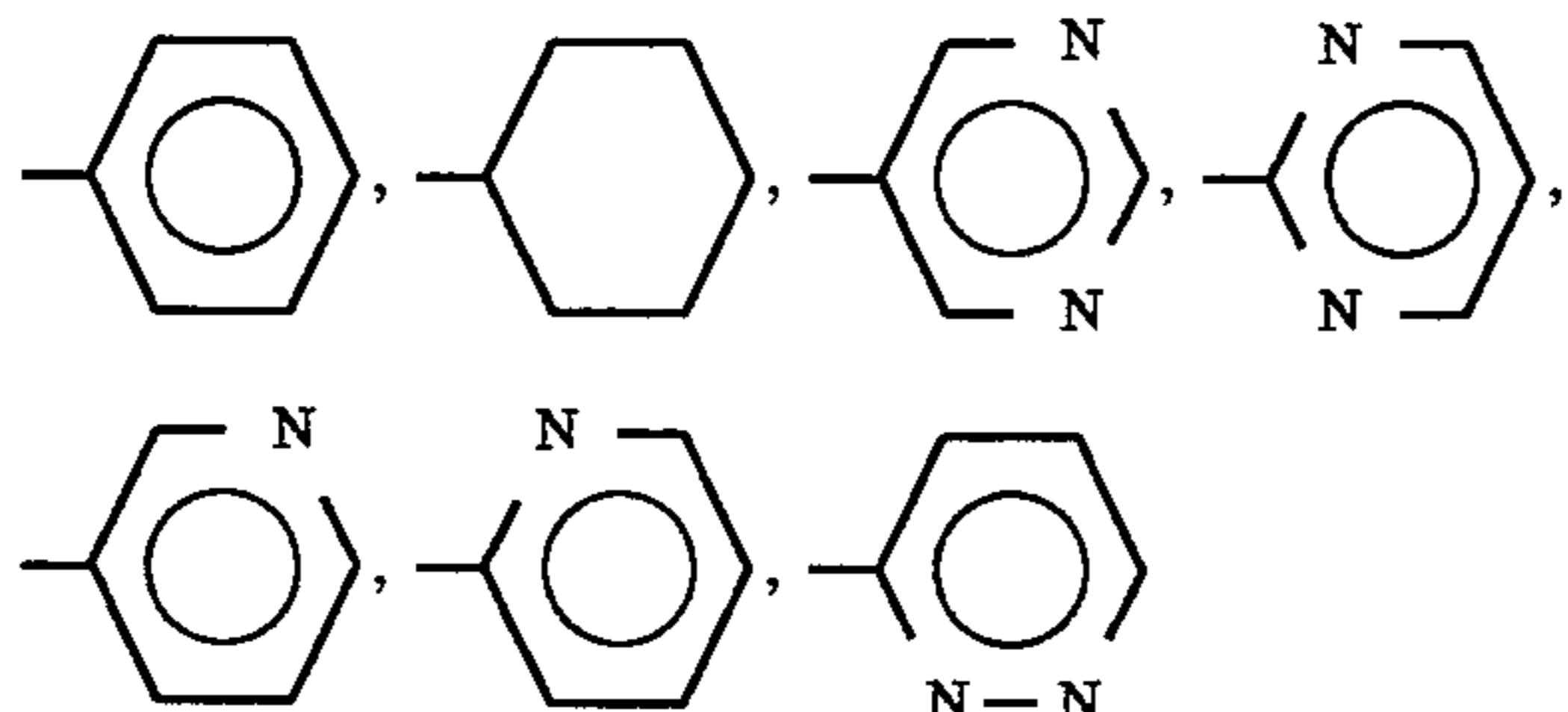
k and m denote zero or 1,

n denotes zero, 1 or 2, with the following proviso: if j and/or l are zero, k is zero; if n is zero, m is zero; the sum J+1+n is at least 1 and at most 3,

---A¹ and ---A² denote

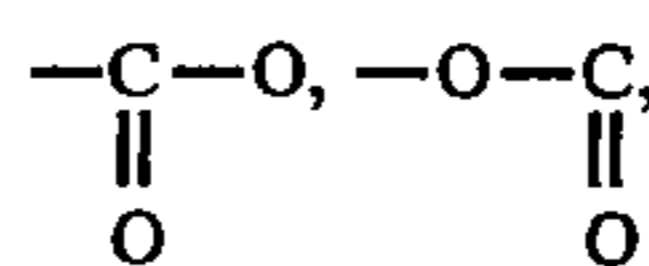


---A³ denotes



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---M¹ and ---M² denote

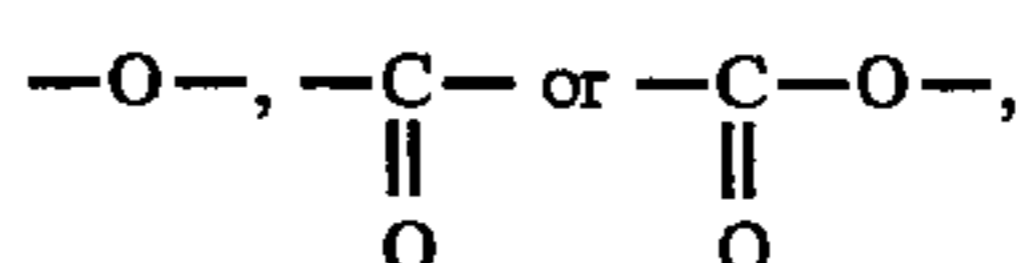


---CH₂CH₂, ---CH=CH, ---CH₂O, ---OCH₂, and

X denotes O or S.

In a preferred embodiment, the symbols in the general formula (I) have the following meaning:

R¹ denotes a straight-chain or branched alkyl or alkenyl radical which has 4 to 14 carbon atoms and which may contain an asymmetrical carbon atom, or where one ---CH₂--- group may be replaced by



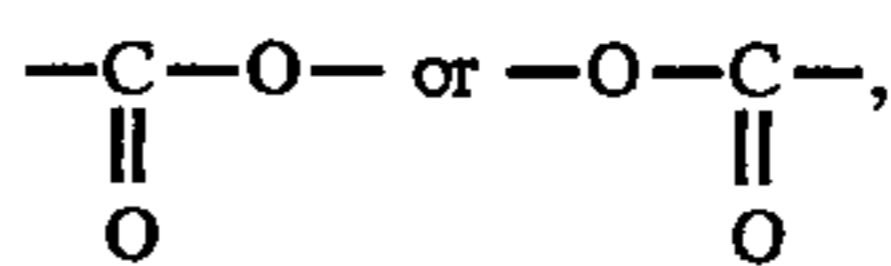
or where one or more H may be replaced by F,

R², R³ and R⁴ denote H or an alkyl radical having 1 to 5 carbon atoms, or R² and R³, together with the C(2) atom or the dioxolane ring, denote a cyclopentane or cyclohexane ring,

j and l denote zero or 1,

k, m and n denote zero or 1,

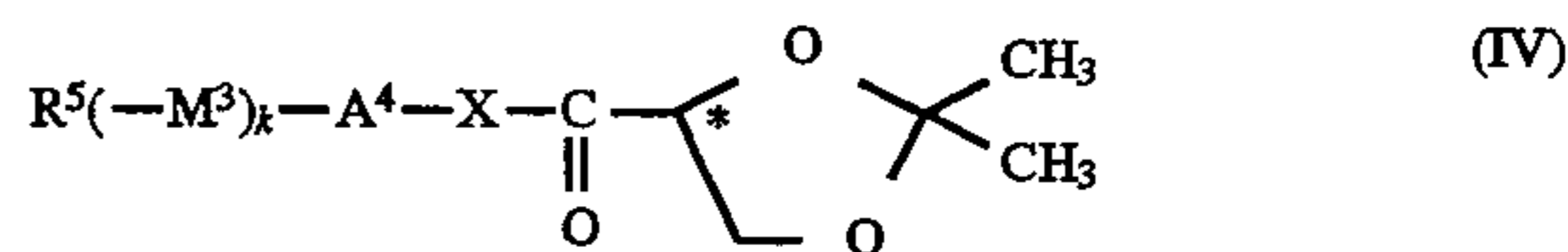
---M¹ and ---M² denote



and

X denotes O or S.

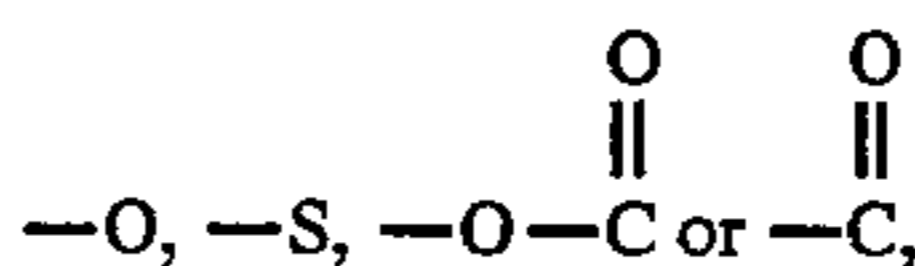
In a further preferred embodiment, 1,3-dioxolane-4-carboxylates of the general formula (IV)



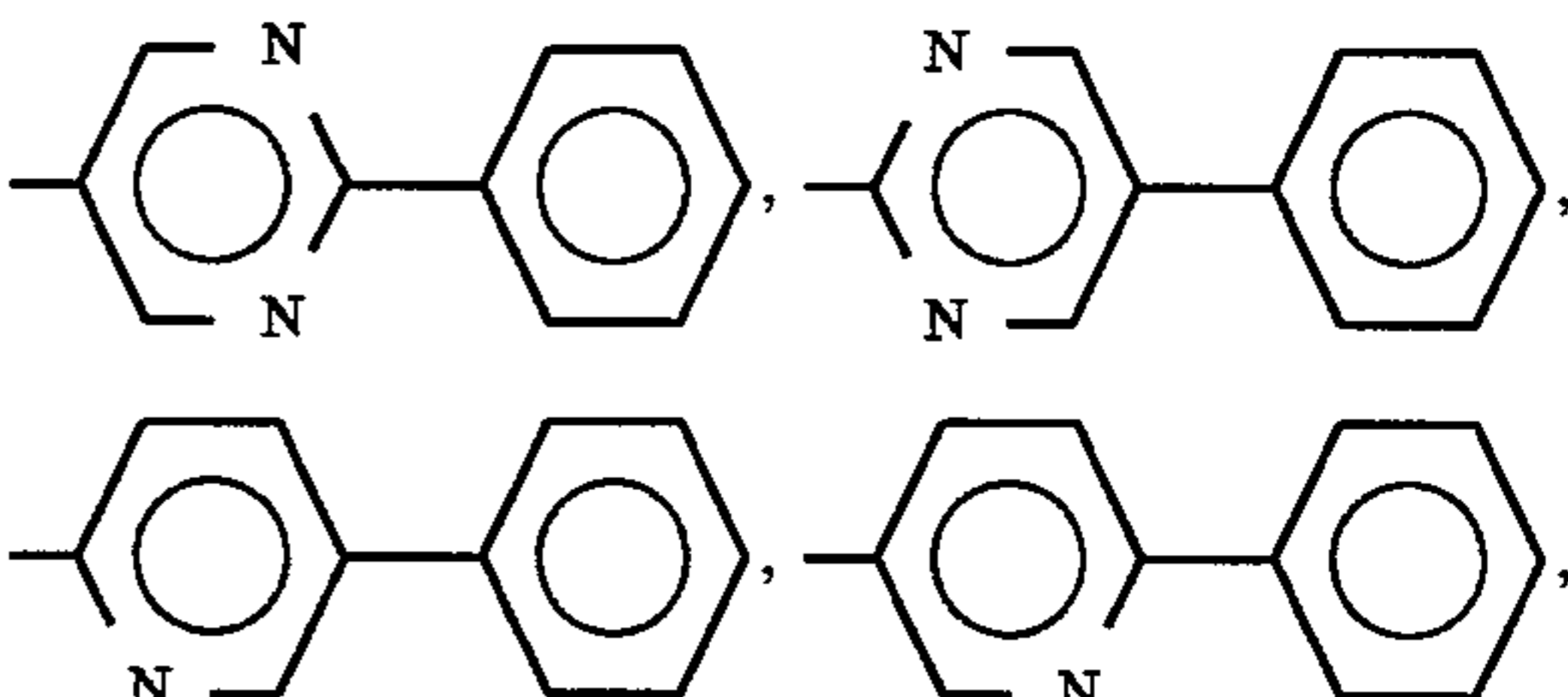
are employed in which:

R⁵ denotes a straight-chain or branched alkyl or alkenyl radical which has 6 to 12 carbon atoms and which may contain an asymmetrical carbon atom,

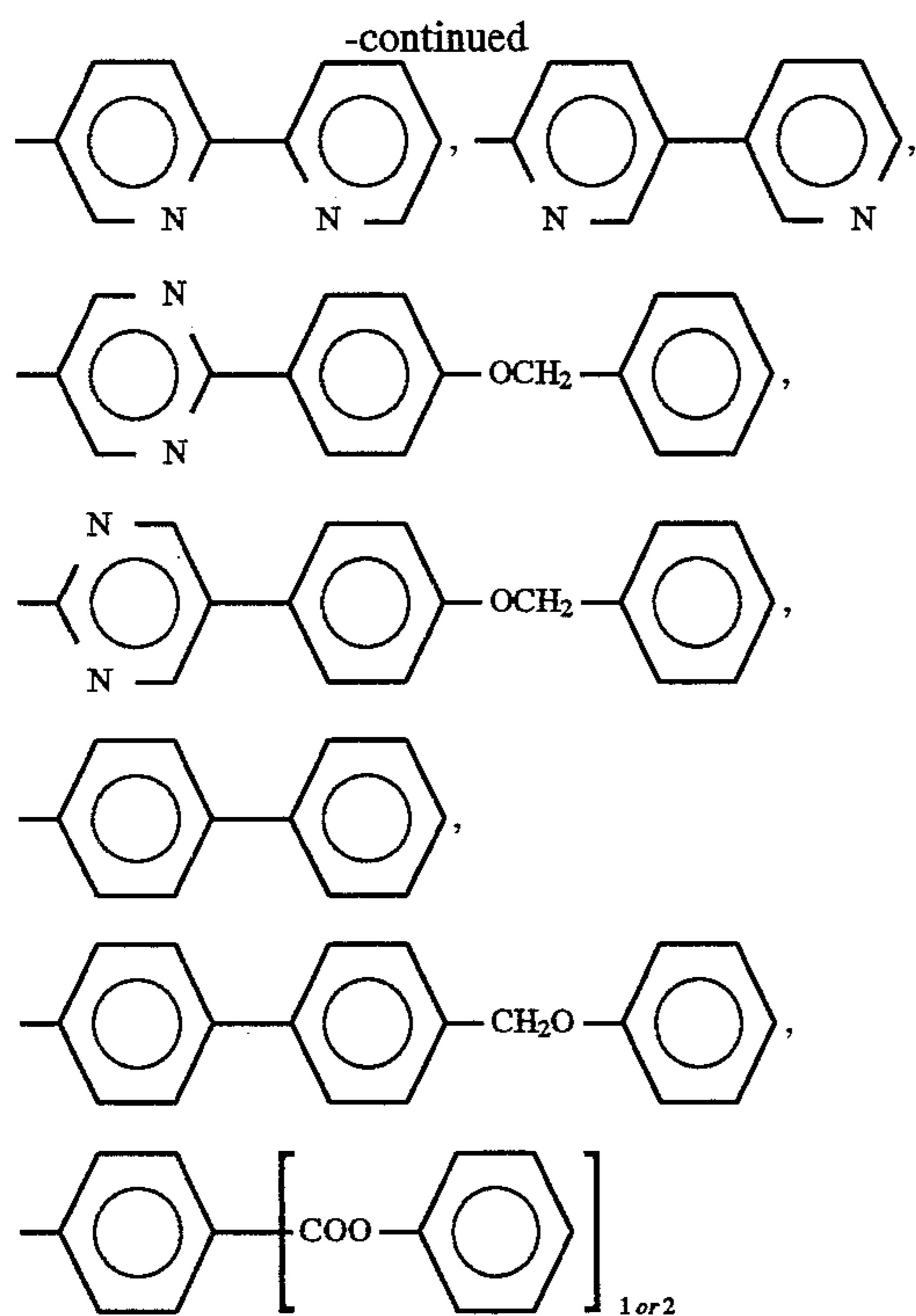
---M denotes



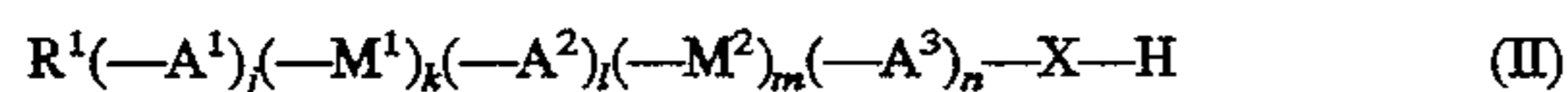
---A⁴ denotes



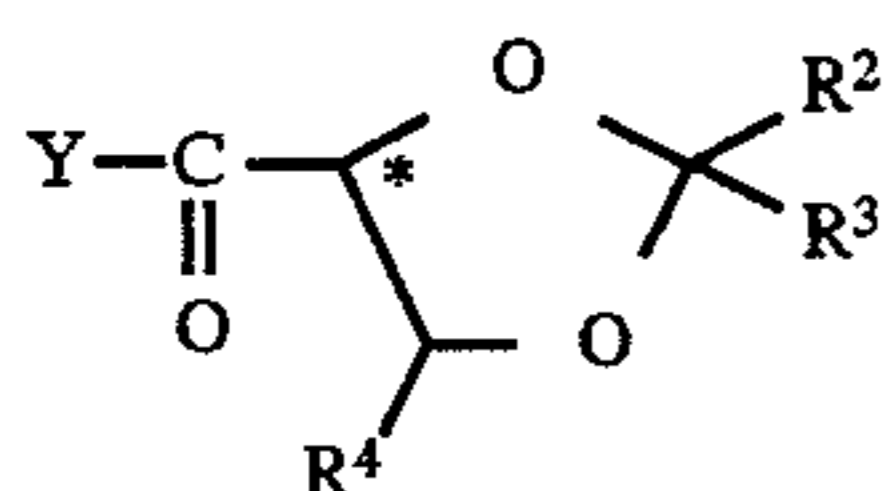
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The novel compounds of the general formula (I), in particular (IV), preferably include the compounds mentioned by name in the examples. For the preparation of compounds of the general formula (I), mesogenic phenols or thiophenols of the general formula (II)



are reacted with suitable derivatives of 1,3-dioxolane-4-carboxylic acid (III), preferably the acyl chlorides (where Y=Cl)



in the presence of equivalent or excess amounts of organic or inorganic bases, if appropriate with the aid of acylating catalysts, in a suitable solvent, and the reaction product is isolated and purified by suitable measures, for example by crystallization, filtration or chromatographic separation methods. Y in this formula is a suitable leaving group, such as Cl, Br, ONa or comparable groups. The phenols to be used are known from the literature. Methods for the preparation of 1,3-dioxolane-4-carboxylic acid derivatives which are suitable in the above sense are likewise known from the literature, for example M. Angrick et al., Monatsheft für Chemie 116, 377 (1985); R. Dumont et al., Helv. Chim. Acta 66, 814 (1983), T. Sugiyama et al., Agric. Biol. Chem. 48, 1841 (1984) or J. Jurczak et al., Tetrahedron 42, 447 (1986). The two components (II) and (III) can be linked to form (I) by methods which are known per se from the literature, such as described, for example, by J. -M. Beau et al., Tetrahedron Letters 26, 6193 (1985).

The liquid-crystal mixtures according to the invention form liquid-crystal phases and contain at least one optically active compound of the general formula (I).

The term "liquid-crystal phase" is taken to mean nematic, cholesteric, orthogonally smectic or tilted smectic phases, in

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particular S^*_A , S^*_B and S^*_C phases. The liquid-crystal mixtures comprise 2 to 20, preferably 2 to 15, components, including at least one of the chiral compounds claimed according to the invention.

The other components are preferably selected from known compounds having nematic, cholesteric and/or smectic phases, for example S_A phases, and/or tilted smectic phases; these include, for example, Schiff bases, biphenyls, terphenyls, phenylcyclohexanes, cyclohexylbiphenyls, N-, S- or O-containing heterocyclic compounds, for example pyrimidines, cinnamates, cholesterol esters and various bridged, multinuclear p-alkylbenzoates with polar terminal groups. In general, the commercially available liquid-crystal mixtures are already present, before addition of the optically active compound(s), as mixtures of a very wide variety of components, of which at least one is mesogenic, i.e. as the compound, in derivatized form or mixed with certain cocomponents, exhibits a liquid-crystal phase which gives expectations of at least one enantiotropic (clear point > melting point) or monotropic (clear point < melting point) mesophase formation. In addition to at least one of the optically active compounds claimed according to the invention, the liquid-crystal mixture contains, in particular, one ester compound having an S_C phase, for example a phenyl alkoxybenzoate, or a biaromatic compound having a nitrogen-containing heterocyclic ring, for example an alkylpyrimidinylalkoxybenzene.

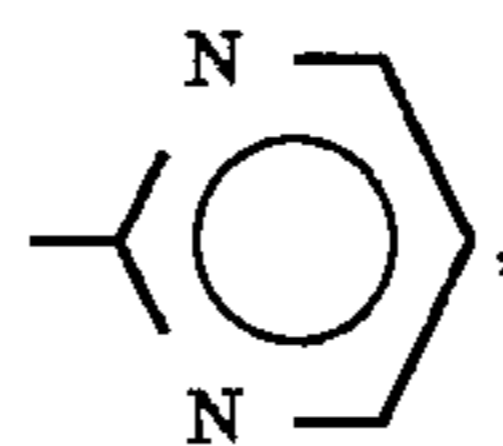
The liquid-crystal mixtures generally contain 0.05 to 70% by weight, in particular 0.1 to 50% by weight, of the compound(s) according to the invention. The compounds according to the invention are suitable, in particular, as dopes for tilted, smectic liquid-crystal phases since they convert the latter into ferroelectric liquid-crystal phases; the values for spontaneous polarization (P_s) at 25° C. are in the range about 8–14 nC/cm² at doping levels of 10 mol-% and in the range about 80–140 nC/cm² linearly extrapolated to the pure compound. The switching times for the novel systems are mostly significantly below 50 μs at doping levels of 10 mol-%, 25° C. and a switching voltage of ±10 V/μm.

The compounds according to the invention can also be employed in order to achieve the electroclinic effect in orthogonal, smectic phases (S^*_A , S^*_B and S^*_E).

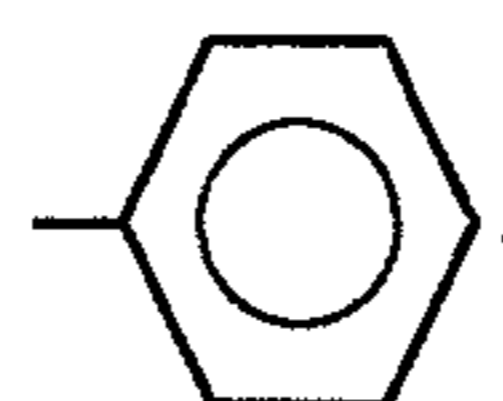
EXAMPLE 1

(R)-4-(2-n-octylpyrimidin-5-yl)phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=C_8H_{17}$, $j=1$, $-A^1=$



$k=l=m=zero$, $n=1$, $-A^3=$



$X=O$, $R^2=R^3=CH_3$ and $R^4=H$].

1.86 g (11.3 mmol) of 2,2-dimethyl-1,3-dioxolane-4-carbonyl chloride are added over the course of 10 minutes to a solution of 3.2 g (11.3 mmol) of 4-(2-n-octylpyrimidin-5-yl)phenol, 1.24 g (12.3 mmol) of triethylamine and 10 mg of

4-dimethylaminopyridine in 30 ml of tetrahydrofuran at 0° C. After the mixture has been stirred for three hours at 0° C, the triethylammonium hydrochloride is filtered off and the filtrate is dried in vacuo.

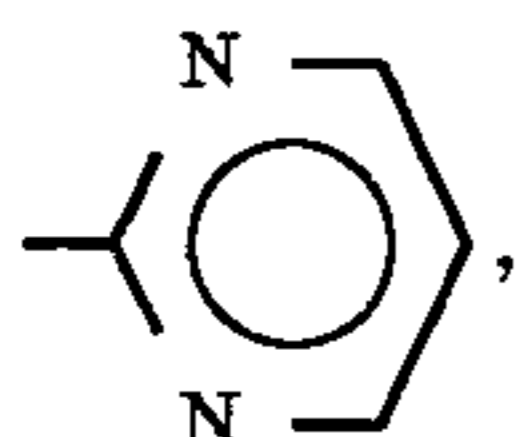
After chromatographic purification and recrystallization from n-hexane, 1.6 g (34.3% of theory) of colorless crystals of melting point 88° C are obtained;

$[\alpha]_D^{21}$: +7.54 (c=5, CDCl₃). The following are obtained analogously

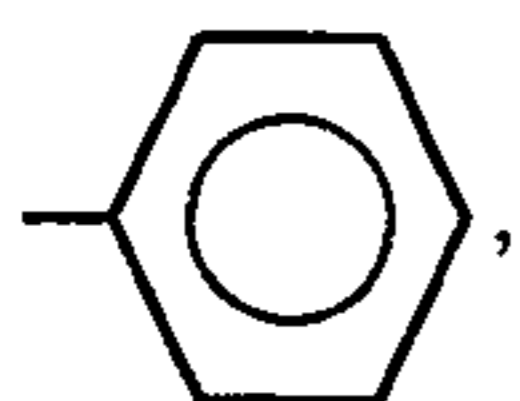
EXAMPLE 2

(R)-4-(2-n-octyloxypyrimidin-5-yl)phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where R¹=H₁₇C₈O, j=1, —A¹=



k=l=m=zero, n=1, —A³=



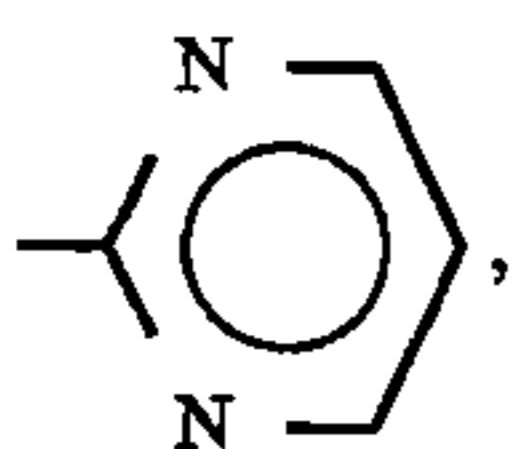
X=O, R²=R³=CH₃, and R⁴=H]

Melting point 85° C. $[\alpha]_D^{20}$: +7.1 (c=1.1, CDCl₃)

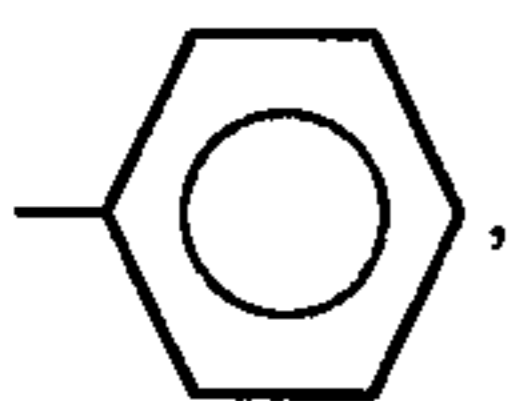
Example 3

(R)-4-(2-n-octylthiopyrimidin-5-yl)phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where R¹=H₁₇C₈S, j=1, —A¹=



k=l=m=zero, n=1, —A³=



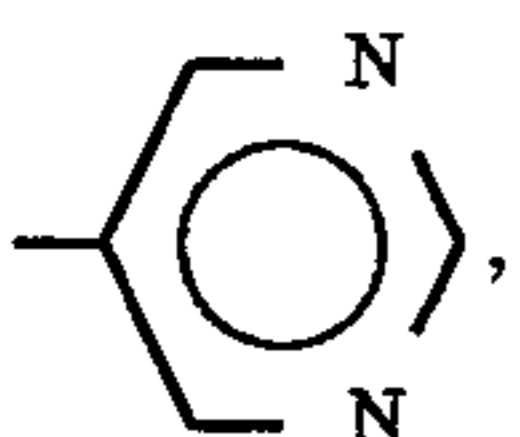
X=O, R²=R³=CH₃, R⁴=H]

Melting point 75° C. $[\alpha]_D^{20}$: +7.8 (c=1.1, CDCl₃).

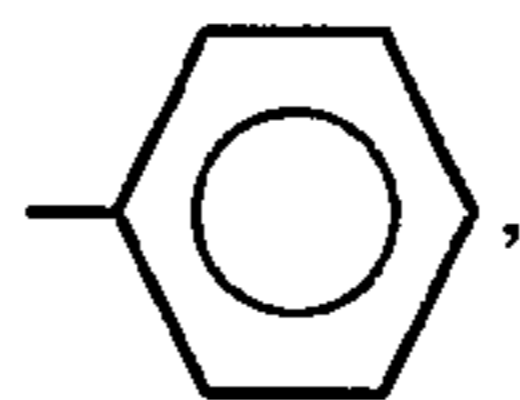
EXAMPLE 4

(R)-4-(5-n-octylpyrimidin-2-yl)phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where R¹=H₁₇C₈, j=1, —A¹=



k=l=m=zero, n=1, —A³=



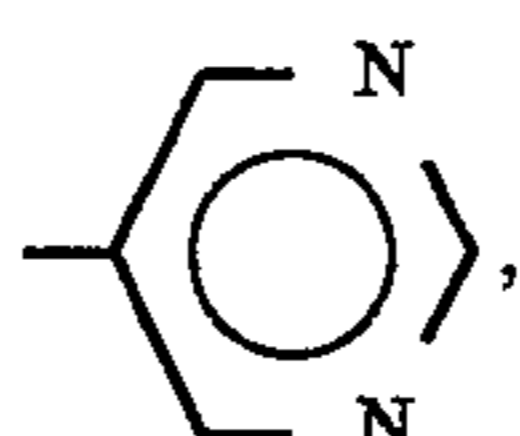
X=O, R²=R³=CH₃, R⁴=H]

Melting point 87° C. $[\alpha]_D^{20}$: 9.0 (c=5, CDCl₃)

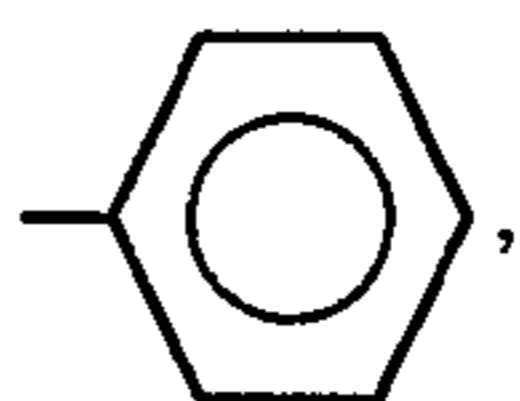
EXAMPLE 5

(R)-4-(5-n-octyloxypyrimidin-2-yl)phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where R¹=H₁₇C₈O, j=1, —A¹=



k=l=m=zero, n=1, —A³=



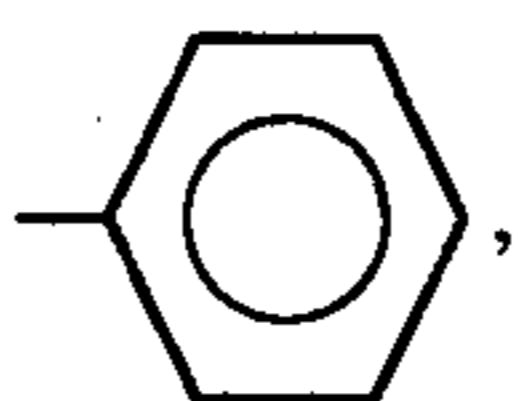
X=O, R²=R³=CH₃, R⁴=H]

Melting point 112° C. $[\alpha]_D^{20}$: +11.0 (c=5, CDCl₃)

EXAMPLE 6

(R)-(4'-octyloxybiphenyl-4-yl) 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where R¹=H₁₇C₈O, j=k=l=m=zero, n=2, —A³=



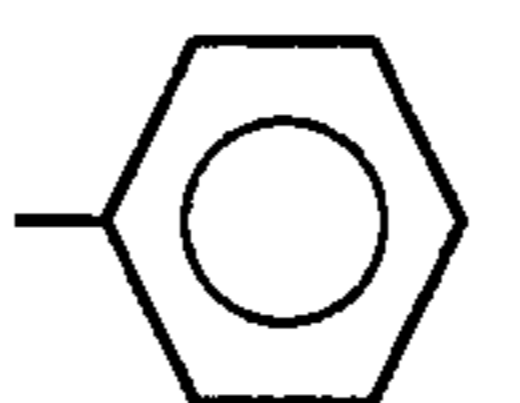
X=O, R²=R³=CH₃ and R⁴=H]

Melting point 115° C. $[\alpha]_D^{20}$: +7.9 (c=1, CDCl₃)

EXAMPLE 7

(R),(R)-4,4'-dihydroxydiphenyl bis(2,2-dimethyl-1,3-dioxolane-4-carboxylate)

[(I) where R¹=2,2-dimethyl-1,3-dioxolane-4-carboxyloxy-, j=k=l=m=zero, n=2, —A³=



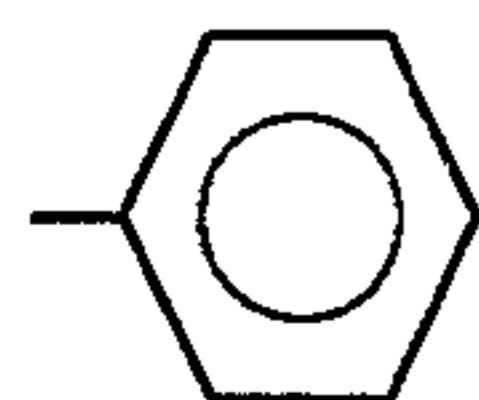
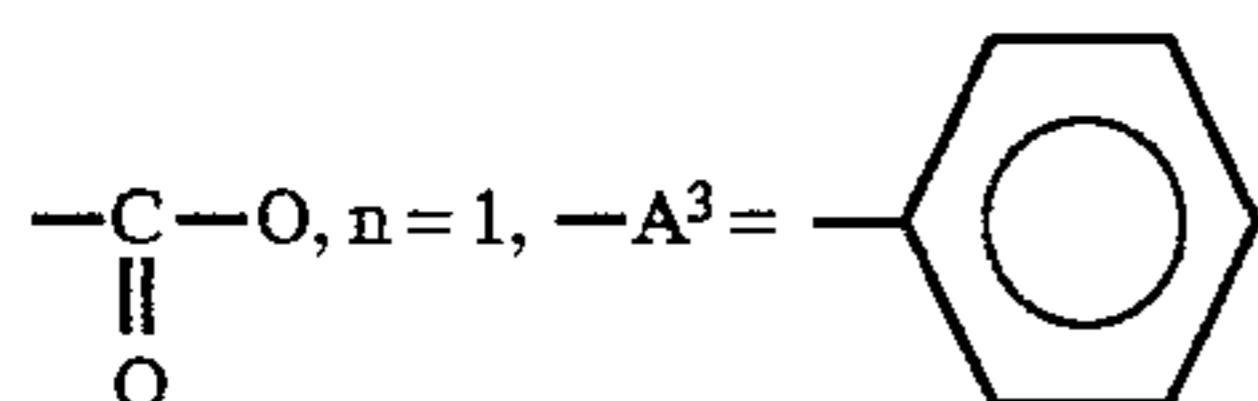
X=O, R²=R³=C₃ and R⁴=H]

Melting point 196° C. $[\alpha]_D^{20}$: +14.7 (c=5, CDCl₃)

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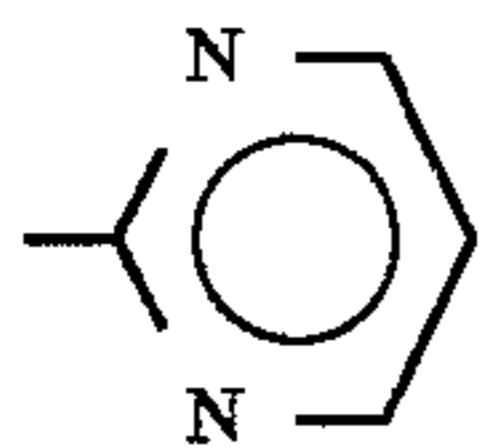
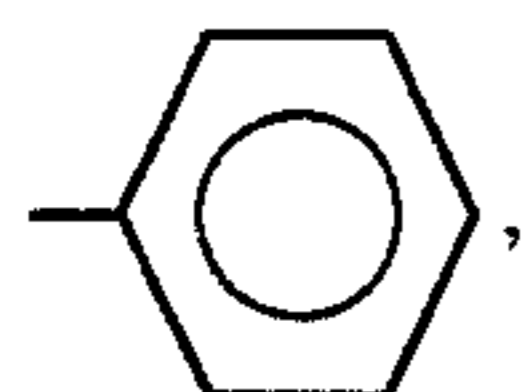
EXAMPLE 8

(R)-[4-(4-decyloxybenzoyloxy)phenyl]2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{21}C_{10}O$, $j=1$, $-A^1=$  $k=l=$ zero, $m=1$, $-M^2=$  $X=O$, $R^2=R^3=CH_3$ and $R^4=H$ Melting point $94^\circ C$. $[\alpha]_D^{20}$: +5.5 ($c=2.2$ $CDCl_3$)

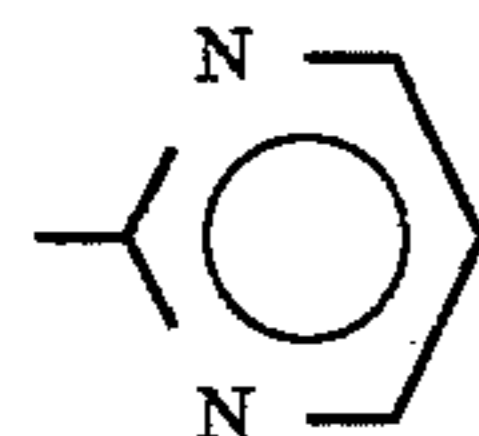
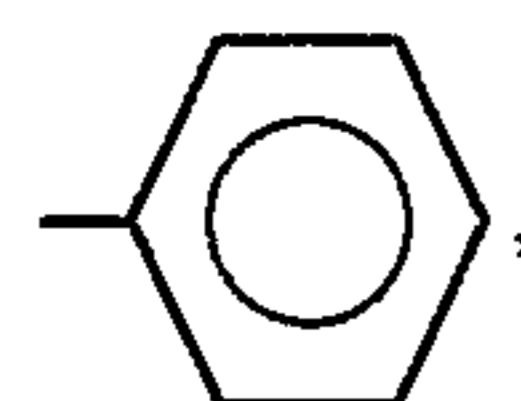
EXAMPLE 9

(R)-4-(2-n-octylthiopyrimidin-5-yl)phenyl 2,2-pentamethylene-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{17}C_8S$, $j=1$, $-A^1=$  $k=l=m=$ zero, $n=1$, $-A^3=$  $X=O$, $R^2+R^3=(CH_2)_5$, $R^4=H$ Melting point $90.8^\circ C$. $[\alpha]_D^{20}$: +15.1 ($c=5$, CH_2Cl_2)

EXAMPLE 10

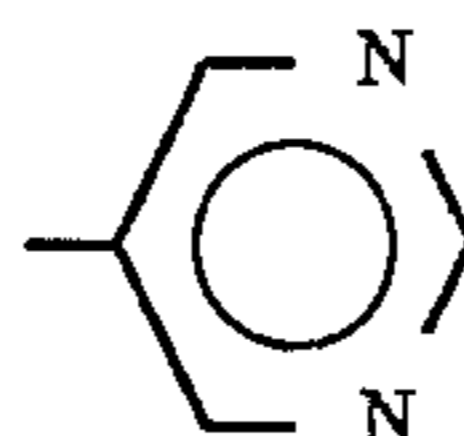
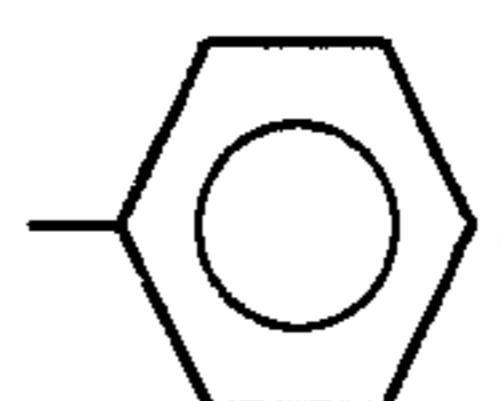
(R)-4-(2-n-octyloxy pyrimidin-5-yl)phenyl 2,2-pentamethylene-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{17}C_8O$, $j=1$, $-A^1=$  $k=l=m=$ zero, $n=1$, $-A^3=$  $X=O$, $R^2+R^3=(CH_2)_5$ and $R^4=H$ Melting point $90.1^\circ C$. $[\alpha]_D^{20}$: +13.6 ($c=5$, CH_2Cl_2)

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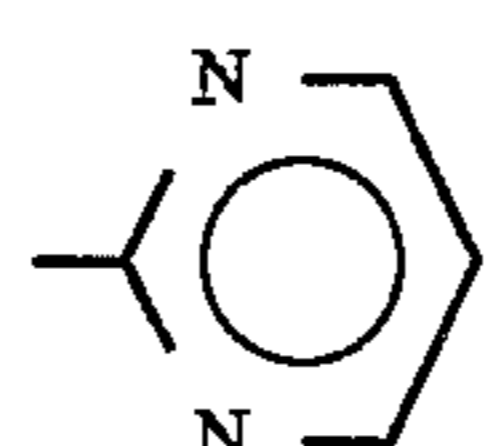
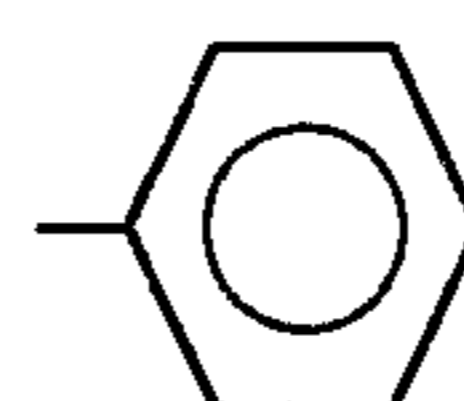
EXAMPLE 11

(R)-4-(5-n-hexylpyrimidin-2-yl)phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{13}C_6$, $j=1$, $-A^1=$  $k=l=m=$ zero, $n=1$, $-A^3=$  $X=O$, $R^2=R^3=CH_3$ and $R^4=H$ Melting point $88.5^\circ C$. $[\alpha]_D^{20}$: +11.0 ($c=7$, $CHCl_3$)

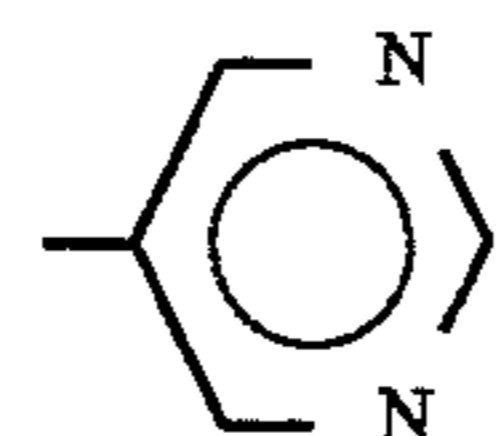
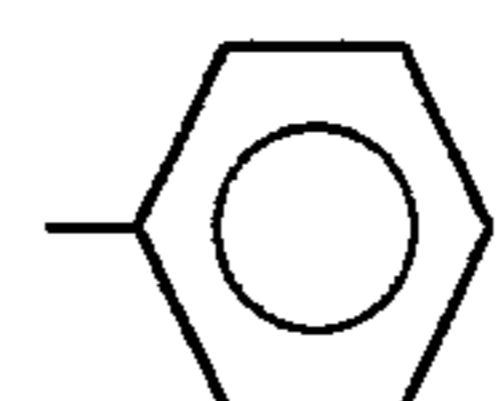
EXAMPLE 12

(R)-4-[2-((S)-7-methylnonyloxy)pyrimidin-5-yl]phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $r^1=H_5C_2CH(CH_3)(CH_2)_6O$, $j=1$, $-A^1=$  $k=l=m=$ zero, $n=1$, $-A^3=$  $X=O$, $R^2=R^3=CH_3$ and $R^4=H$ Melting point $76^\circ C$. $[\alpha]_D^{20}$: +10.2 ($c=5$, CH_2Cl_2)

EXAMPLE 13

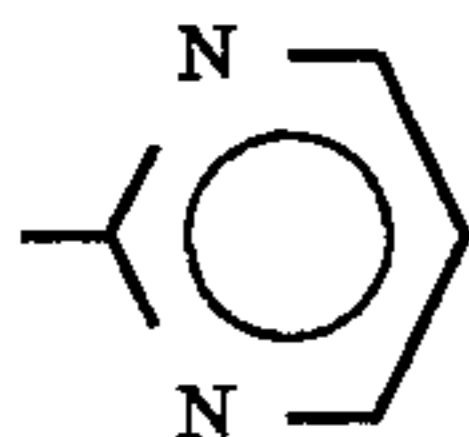
(R)-4-(5-n-octylpyrimidin-2-yl)phenyl 2,2-pentamethylene-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{17}C_8$, $j=1$, $-A^1=$  $k=l=m=$ zero, $n=1$, $-A^3=$  $X=O$, $R^2+R^3=(CH_2)_5$ and $R^4=H$ Melting point $96.8^\circ C$. $[\alpha]_D^{20}$: +16.6 ($c=5$, CH_2Cl_2)

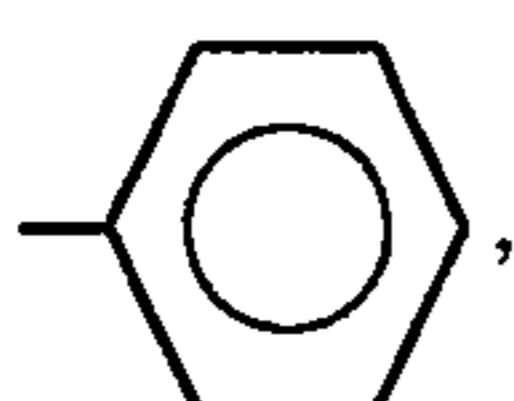
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EXAMPLE 14

(R)-4-(2-n-octylpyrimidin-5-yl)phenyl 2,2-pentamethylene-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{17}C_8$, $j=1$, $-A^1=$



$k=l=m=$ zero, $n=1$, $-A^3=$

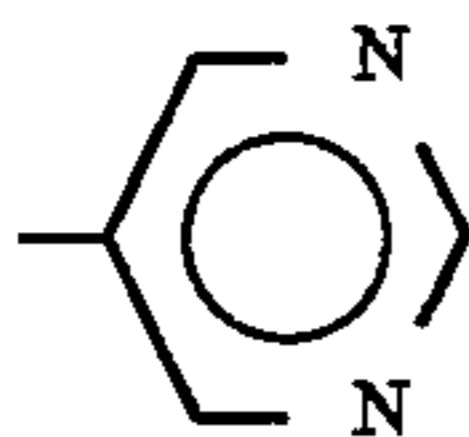


$X=O$, $R^2+R^3=(CH_2)_5$ and $R^4=HMelting point $85.4^\circ C$. $[\alpha]_D^{20}$: +15.0 ($c=5$, CH_2Cl_2)$

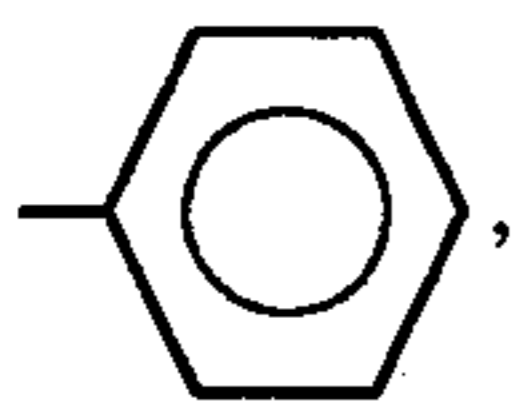
EXAMPLE 15

(R)-4-(5-n-nonylpyrimidin-2-yl)phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{19}C_9$, $j=1$, $-A^1=$



$k=l=m=$ zero, $n=1$, $-A^3=$

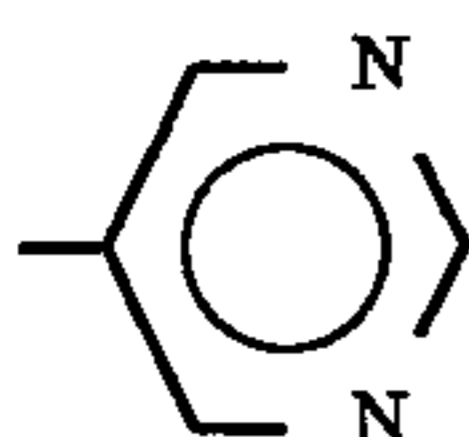


$X=O$, $R^2=R^3=CH_3$ and $R^4=HMelting point $92.4^\circ C$. $[\alpha]_D^{20}$: +8.8 ($c=7.5$, $CHCl_3$)$

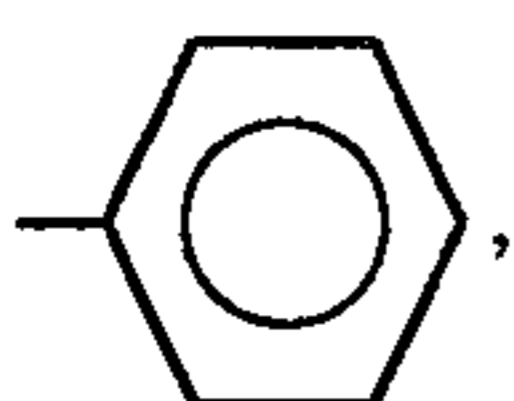
EXAMPLE 16

(R)-4-(5-n-decylpyrimidin-2-yl)phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{21}C_{10}$, $j=1$, $-A^1=$



$k=l=m=$ zero, $n=1$, $-A^3=$

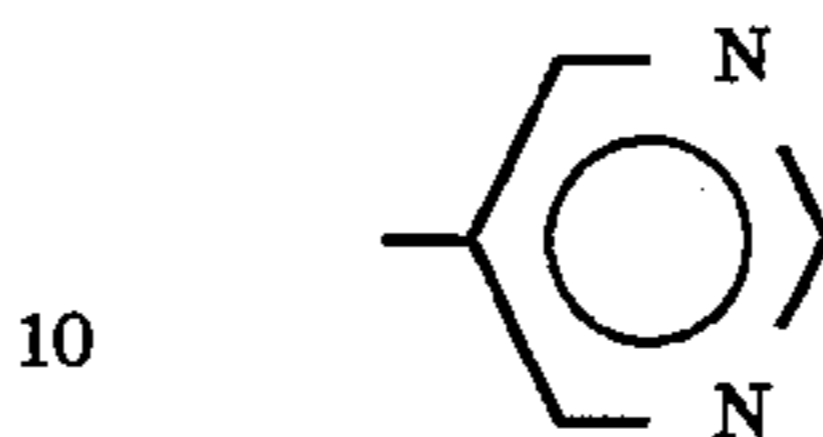


$X=O$, $R^2=R^3=CH_3$ and $R^4=HMelting point $88^\circ C$. $[\alpha]_D^{20}$: +9.2 ($c=5$, $CHCl_3$)$

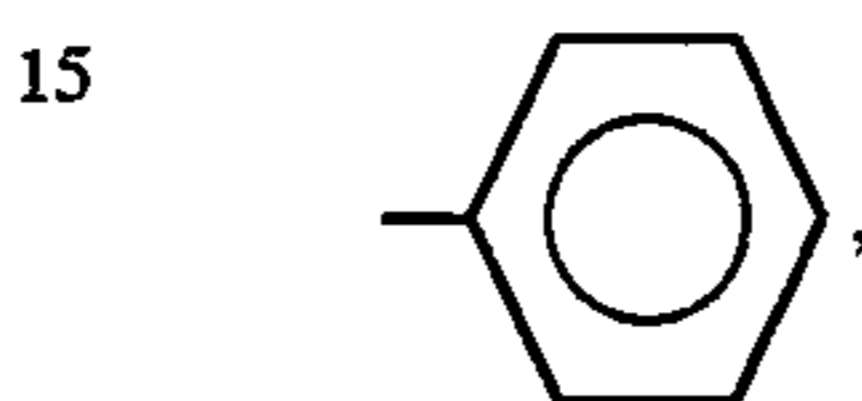
12
EXAMPLE 17

(R)-4-(5-n-undecylpyrimidin-2-yl)phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

5 [(I) where $R^1=H_{23}C_{11}$, $j=1$, $-A^1=$



10 $k=l=m=$ zero, $n=1$, $-A^3=$

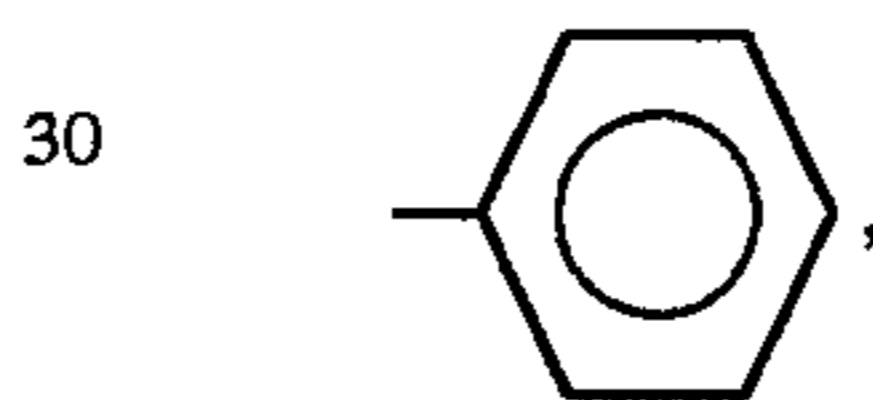


15 $X=O$, $R^2=R^3=CH_3$ and $R^4=H20 Melting point $89.7^\circ C$. $[\alpha]_D^{20}$: +9.6 ($c=5$, $CHCl_3$)$

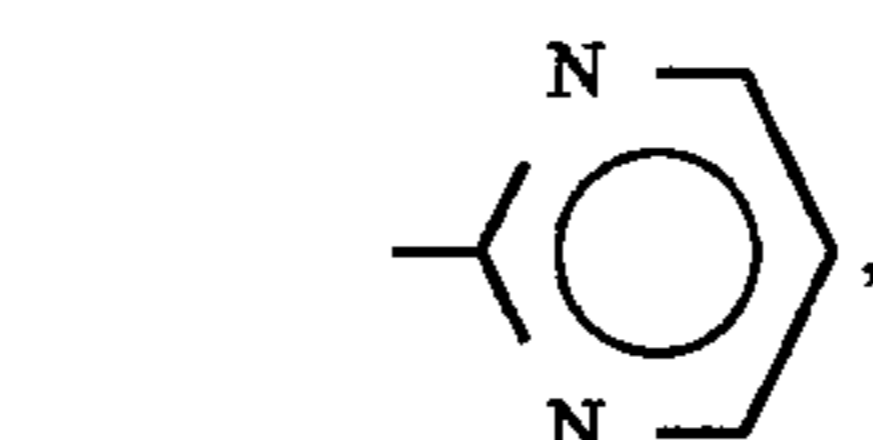
EXAMPLE 18

25 (R)-4-[2-(4-hexylphenyl)pyrimidin-5-yl]phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{13}C_6$, $j=l=n=1$, $k=m=$ zero, $-A^1=-A^3=$



30 $-A^2=$

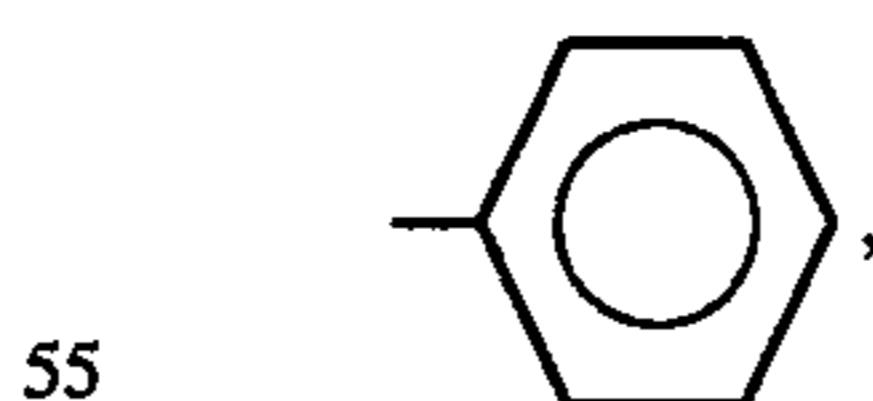


35 $R^2=R^3=CH_3$ and $R^4=HPhase sequence $C 159^\circ S_3 173^\circ S_C 190^\circ S_A 196^\circ I$
40 $[\alpha]_D^{20}$: +8.7 ($C=2$, $CHCl_3$)$

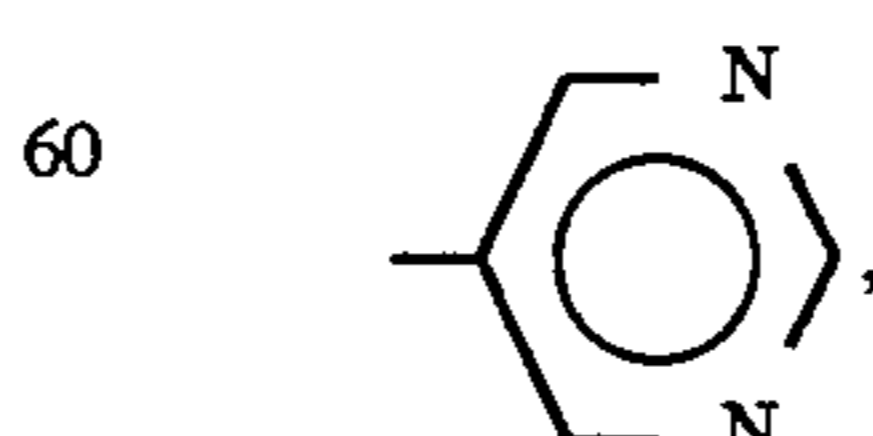
EXAMPLE 19

(R)-4-[5-(4-hexylphenyl)pyrimidin-2-yl]phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

50 [(I) where $R^1=H_{13}C_6$, $j=1=n=1$, $k=m=$ zero, $-A^1=-A^3=$



55 $-A^2=$



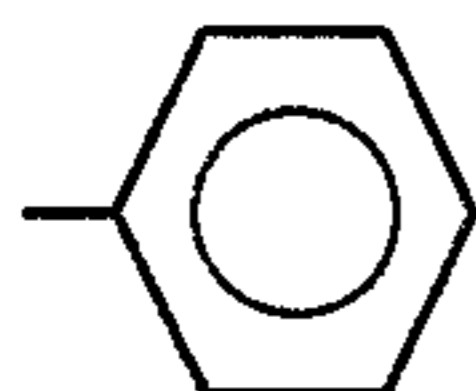
60 $X=O$, $R^2=R^3=CH_3$ and $R^4=H65 Phase sequence $157^\circ S_3 162^\circ S_C 178^\circ S_A 195^\circ I$ $[\alpha]_D^{20}$: +10.1 ($c=2$, $CHCl_3$)$

13

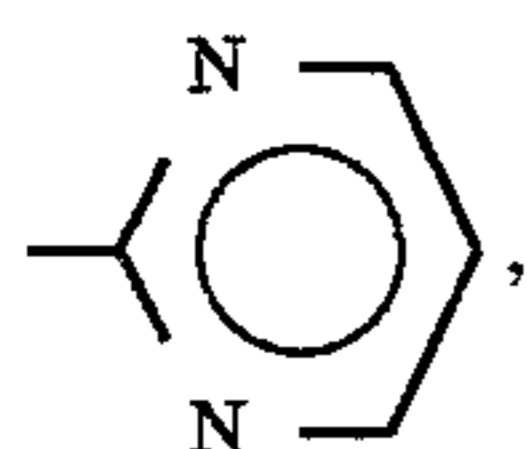
EXAMPLE 20

(R)-[2-(4-dodecyloxyphenyl)]pyrimidin-5-yl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{25}C_{12}O$, $j=1$, $-A^1=$



$l=m=zero$, $-A^3=$



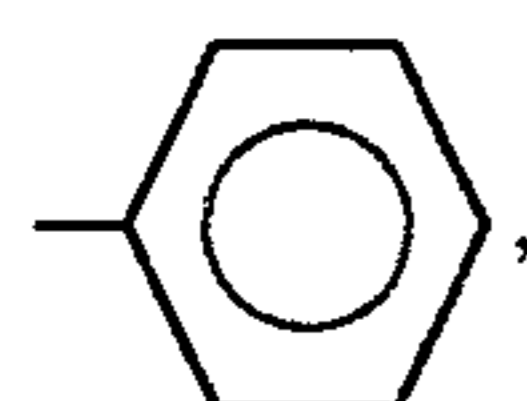
$X=O$, $R^2=R^3=CH_3$ and $R^4=H$

Melting point $97^\circ C$. $[\alpha]_D^{20}$: +6.9 ($c=2$ $CHCl_3$)

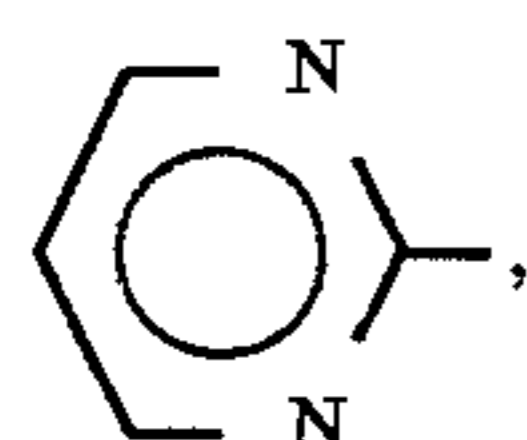
EXAMPLE 21

(R)-[2-<4-(5-oxohexyl)oxyphenyl>]pyrimidin-5-yl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_3C(C=O)(CH_2)_4O$, $j=1$, $-A^1=$



$k=l=m=zero$, $n=1$, $-A^3=$



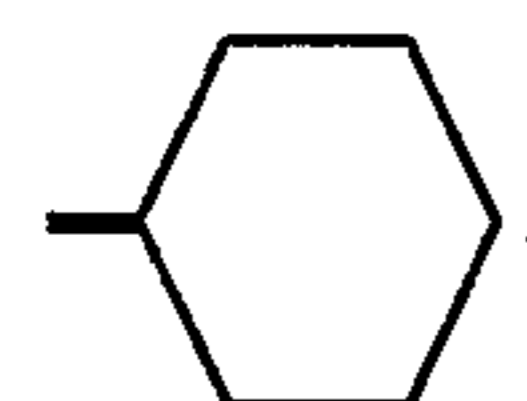
$X=O$, $R^2=R^3=CH_3$ and $R^4=H$

Melting point $139^\circ C$. $[\alpha]_D^{20}$: +7.9 ($c=2$, $CHCl_3$)

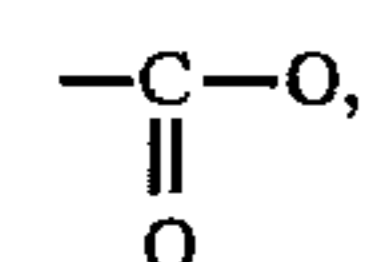
EXAMPLE 22

(R)-[2-<4-(4-trans-pentylcyclohexyl) carbonyloxyphenyl>]pyrimidin-5-yl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{11}C_5$, $j=k=l=n=1$, $m=zero$, $-A^1=$

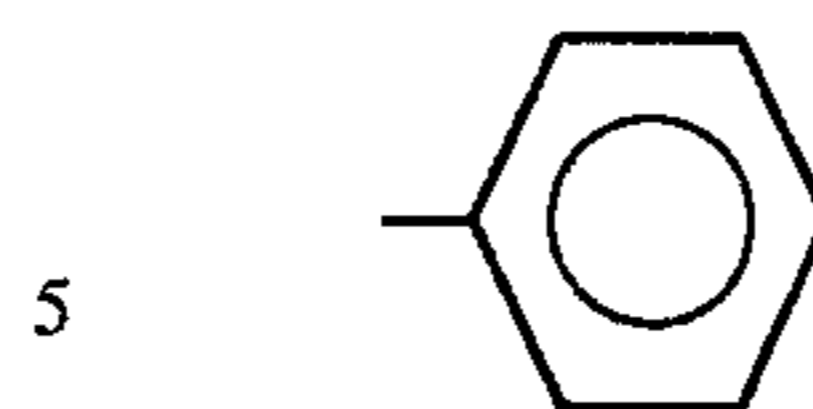


$-M^1=$

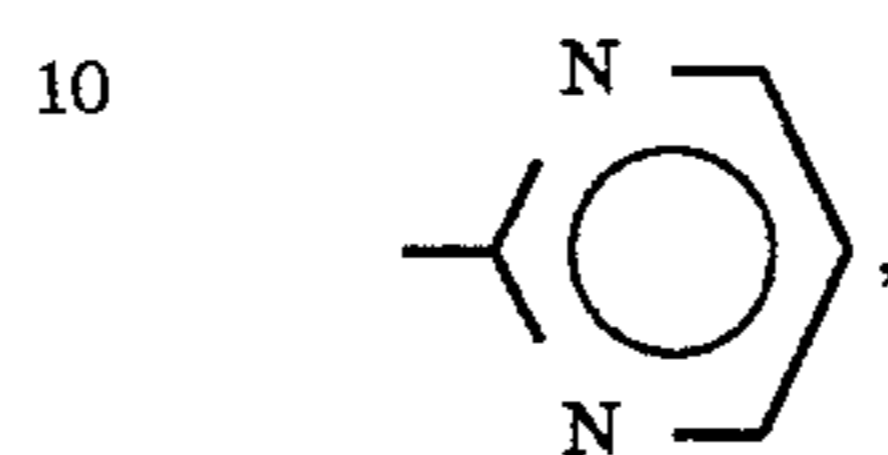


14

$-A^2=$



$-A^3=$



15 $X=O$, $R^2=R^3=CH_3$ and $R^4=H$

Phase sequence C 154° N* 204° I

$[\alpha]_D^{20}$: +6.6 ($c=2$, $CHCl_3$)

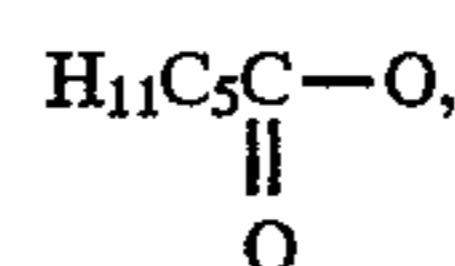
EXAMPLE 23

20

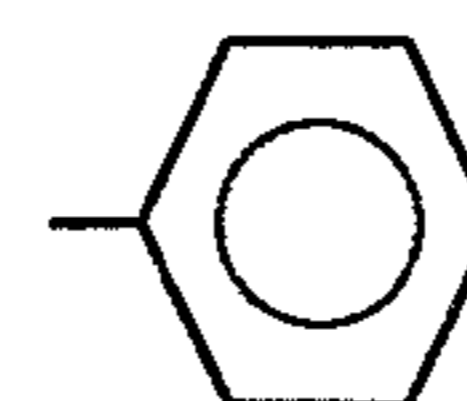
(R)-[2-(4-pentylcarbonyloxyphenyl)]pyrimidin-5-yl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=$

25

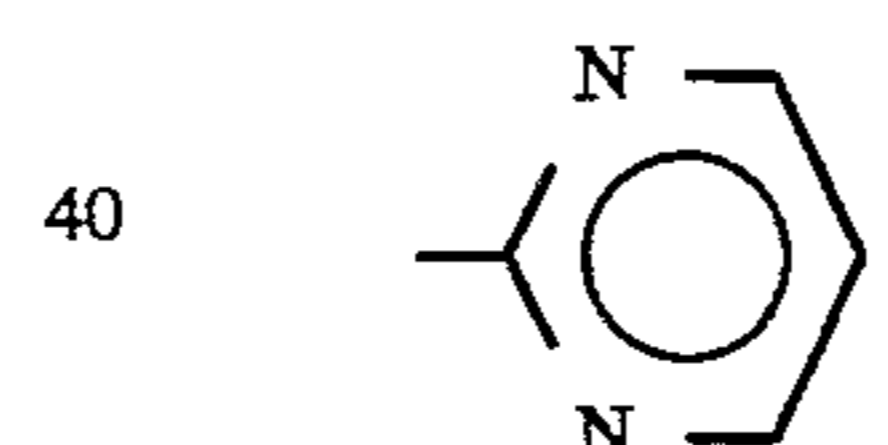


30 $j=1$, $-A^1=$



35

$k=l=m=zero$, $n=1$, $-A^3=$



45 $X=O$, $R^2=R^3=CH_3$ and $R^4=H$

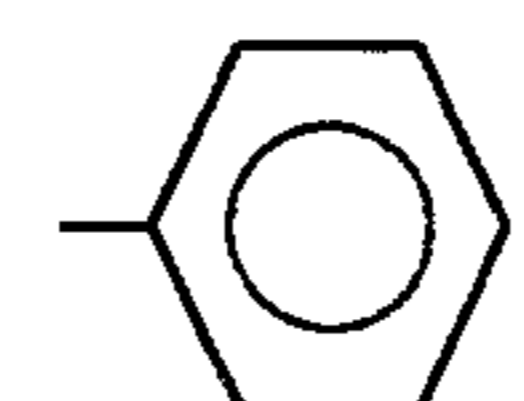
Melting point $115.5^\circ C$. $[\alpha]_D^{20}$: +8.4 ($c=2$, $CHCl_3$)

EXAMPLE 24

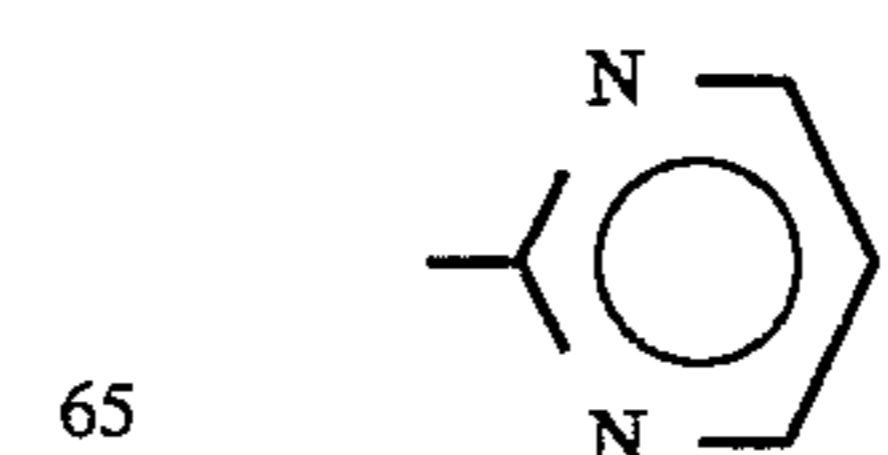
50 (R)-[4-<2-(4-decyloxyphenyl) methyleneoxy pyrimidin-5-yl>]phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{21}C_{10}O$, $j=k=l=n=1$, $m=zero$, $-A^1=$

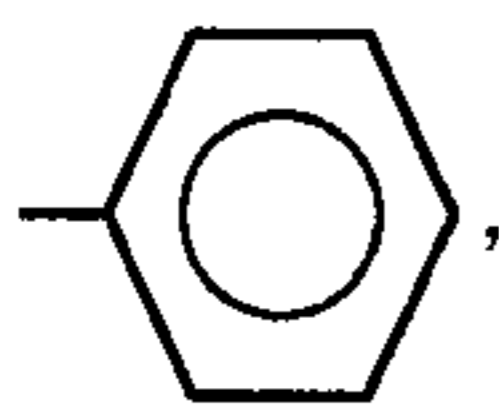
55



60 $-M^1=-CH_2O$, $-A^2=$

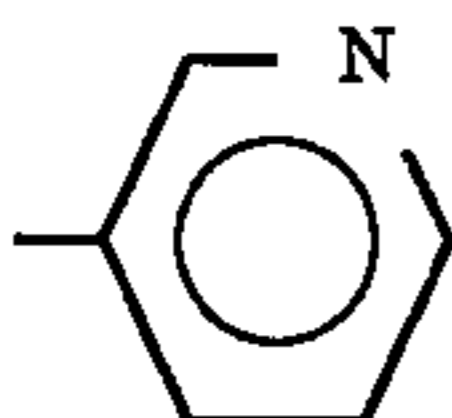
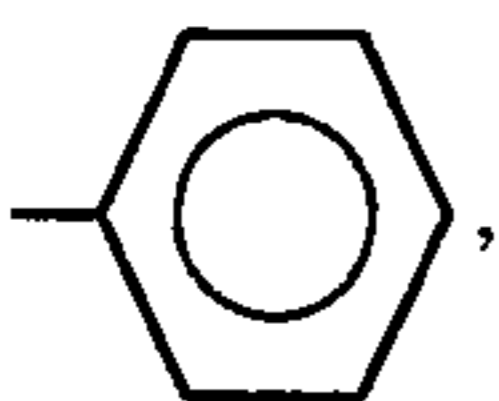


15

 $-A^3=$  $X=O, R^2=R^3=CH_3$ and $R^4=H$ Phase sequence C 107° S_A 125° I $[\alpha]_D^{20}: +5.7$ (c=2, CH₂Cl₂)

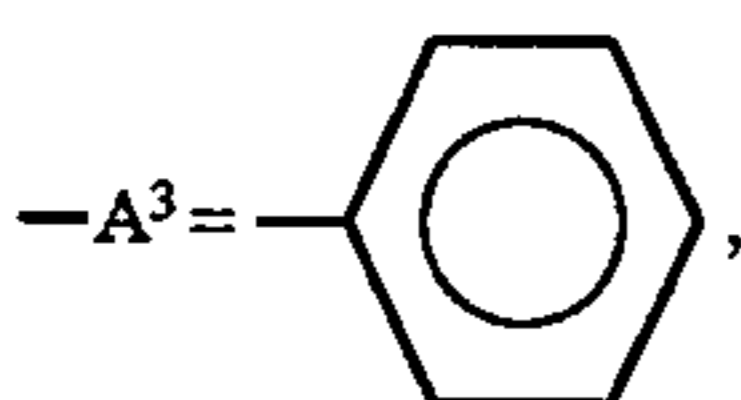
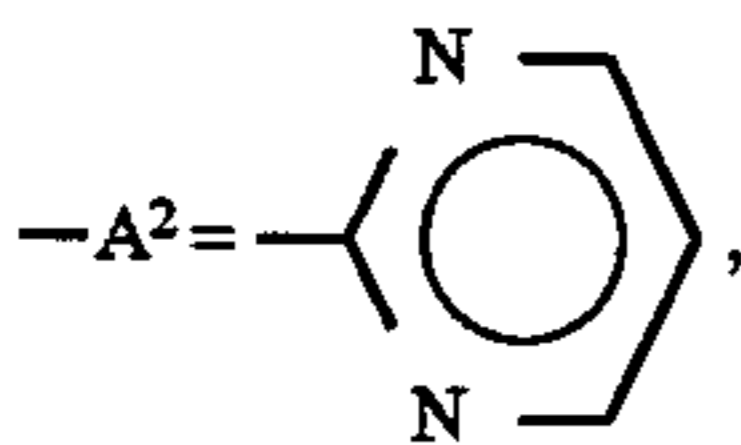
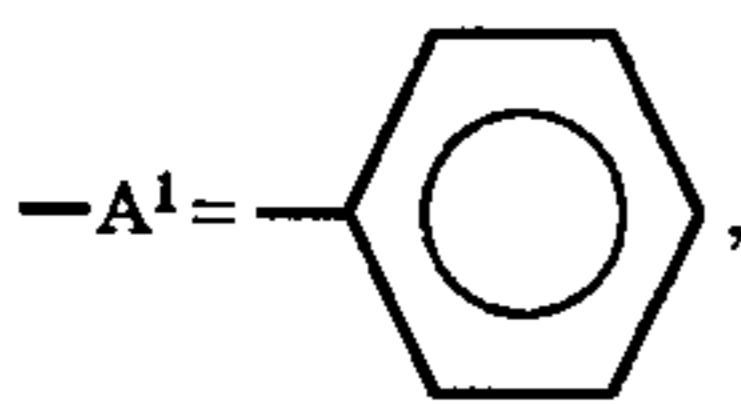
EXAMPLE 25

(R)-[2-(5-octylpyrid-2-yl)]phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{17}C_8, j=1, -A^1=$  $k=l=m=zero, n=1, -A^3=$  $X=O, R^2=R^3=CH_3$ and $R^4=H$ Melting point 107° C. $[\alpha]_D^{20}: +10.1$ (c=2, CHCl₃)

EXAMPLE 26

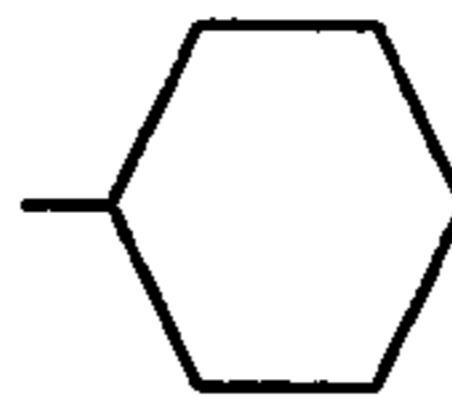
(R)-4-[2-(4-hexyloxyphenyl)pyrimidin-5-yl]phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{13}C_6O, j=1=n=1, k=m=zero,$  $X=O, R^2=R^3=CH_3$ and $R^4=H$ Clear point 209° C. $[\alpha]_D^{20}: +7.9$ (c=2, CHCl₃)

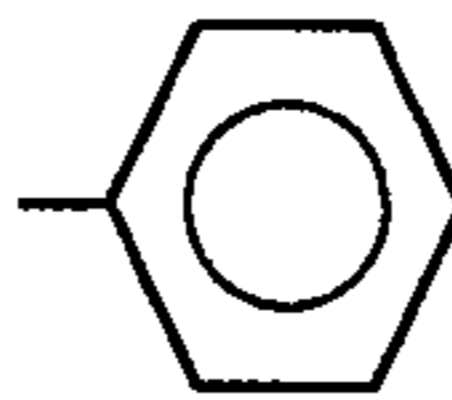
16

EXAMPLE 27

(R)-[4-(4-trans-propylcyclohexyl)]phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

5 [(I) where $R^1=H_7C_3, j=1, -A^1=$ 

10

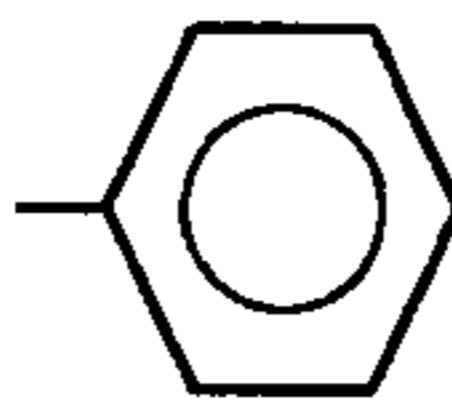
 $k=l=m=zero, n=1, -A^3=$ 

15

20 $X=O, R^2=R^3=CH_3$ and $R^4=H$
Melting point 99.1° C. $[\alpha]_D^{20}: +7.1$ (c=2, CHCl₃)

EXAMPLE 28

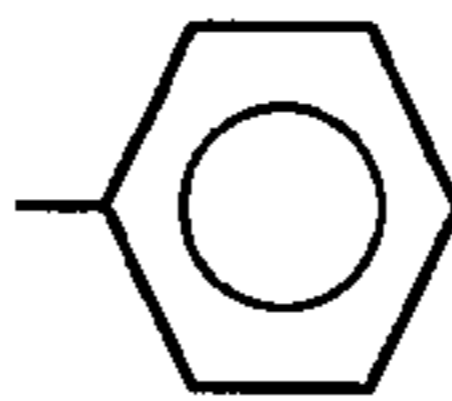
25 (R)-[4'-(4-octyloxybenzoyloxy)]biphenyl-4-yl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

[(I) where $R^1=H_{17}C_8O, j=k=l=1, -A^3=$ 

30

 $-M^1=C-O, l=m=zero, n=2, -A^3=$

35

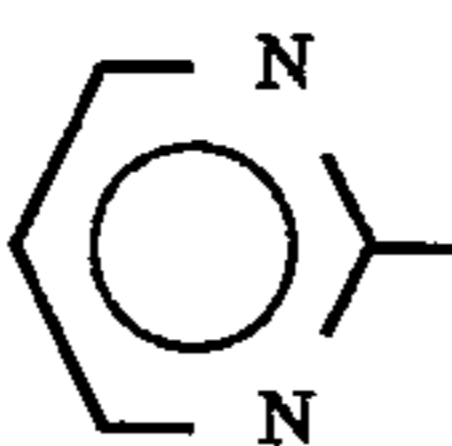


40

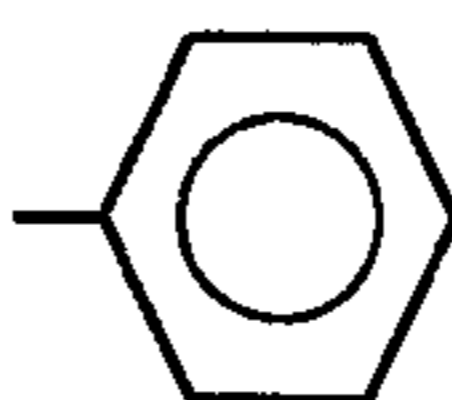
 $X=O, R^2=R^3=CH_3$ and $R^4=H$
Phase sequence C 146.5° S_A 165.5° N* 200.5° I
 $[\alpha]_D^{20}: +5.75$ (c=2, CHCl₃)

EXAMPLE 29

45 (R)-[4-<2-(1,1-H-perfluorooctyl)oxypyrimidin-5-yl>]phenyl 2,2-dimethyl-1,3-dioxolane-4-carboxylate

50 [(I) where $R^1=F_{15}C_7CH_2O, j=1, -A^1=$ 

55

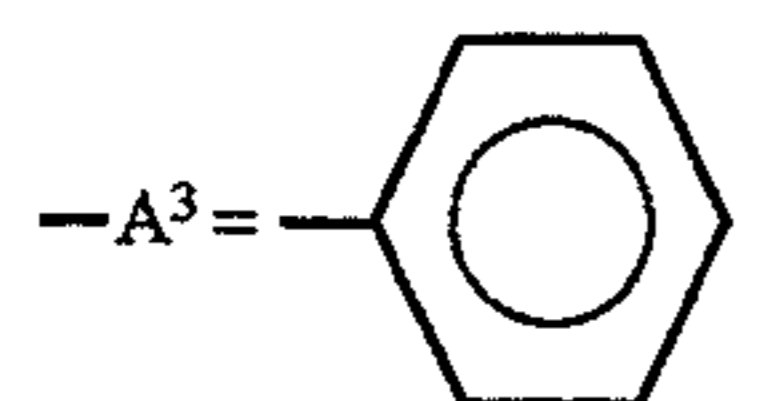
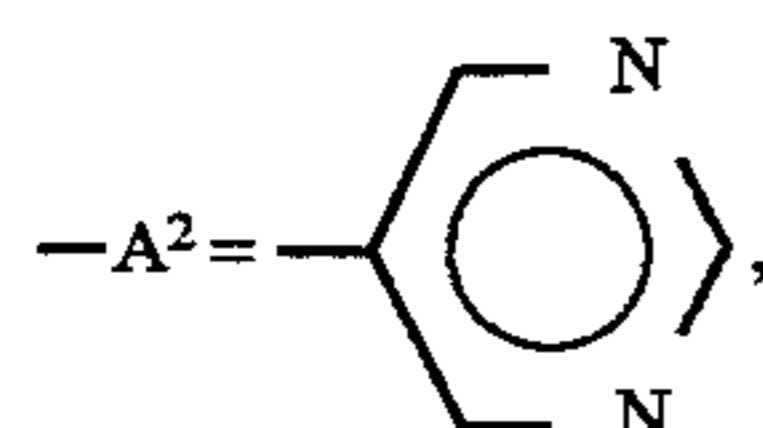
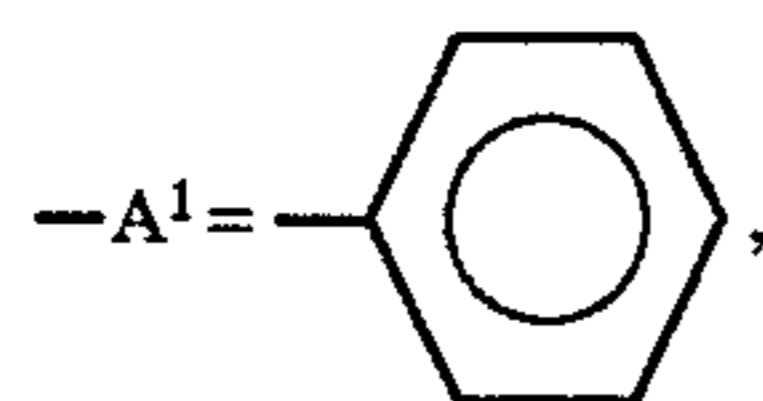
 $k=l=m=zero, n=1, -A^3=$ 

60

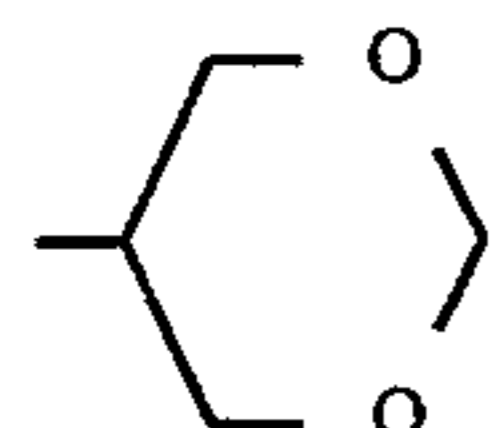
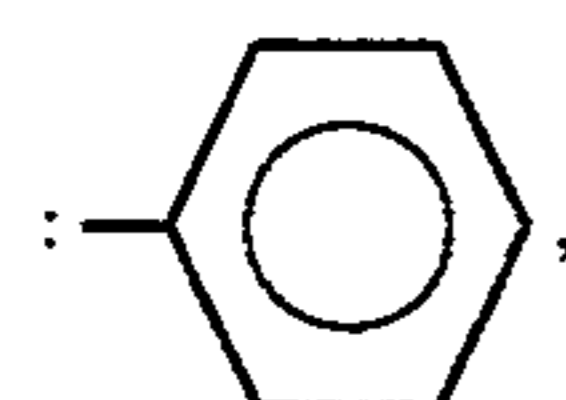
65 $X=O, R^2=R^3=CH_3$ and $R^4=H$
Phase sequence C 107° S_A 125° I
 $[\alpha]_D^{20}: +3.9$ (c=2, CH₂Cl₂)

17

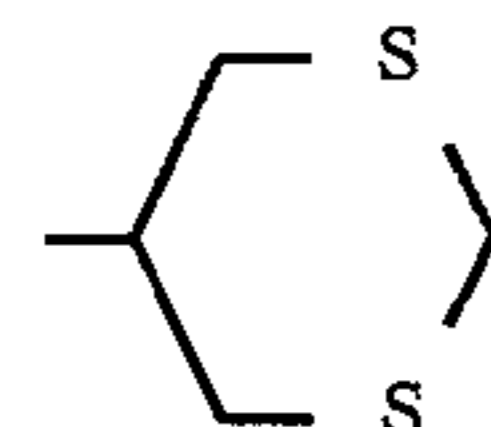
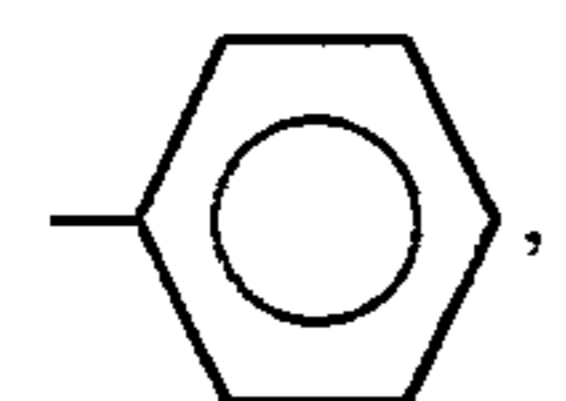
EXAMPLE 30

(R)-4-[5-(4-hexyloxyphenyl)pyrimidin-2-yl]phenyl
2,2-dimethyl-1,3-dioxolane-4-carboxylate[(I) where $R^1=C_{13}H_6O$, $j=l=n=1$, $k=m=zero$, $X=O$, $R^2=R^3=CH_3$ and $R^4=H$ Clear point 213°C . $[\alpha]_D^{20}$: +5.9 ($c=2$, $CHCl_3$)

EXAMPLE 31

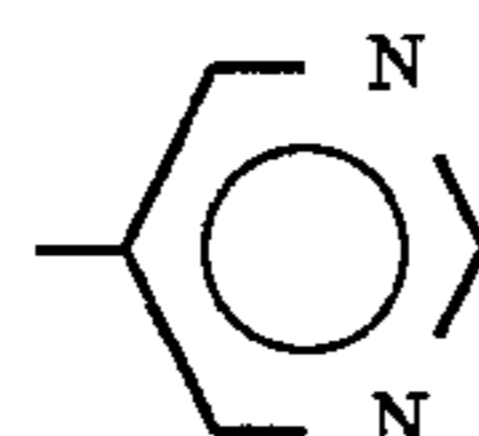
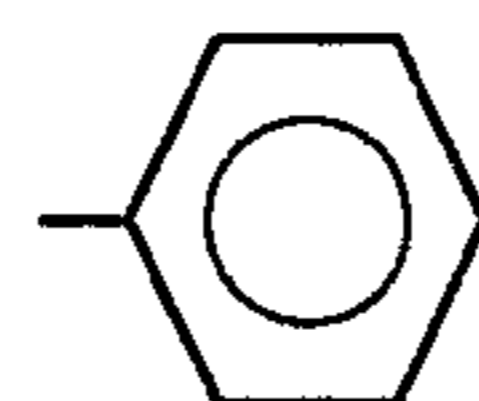
(R)-[4-(5-octyl-1,3-dioxan-2-yl)phenyl]2,2-
dimethyl-1,3-dioxolane-4-carboxylate[(I) where $R^1=H_{17}C_8$, $j=1$, $-A^1=$  $k=l=m=zero$, $n=1$, $-A^3=$  $X=O$, $R^2=R^3=CH_3$ and $R^4=H$ Melting point C 104.3°C . $[\alpha]_D^{20}$: +5.9 ($c=2$, $CHCl_3$)

EXAMPLE 32

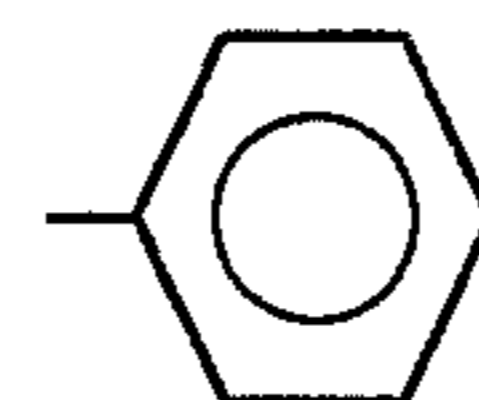
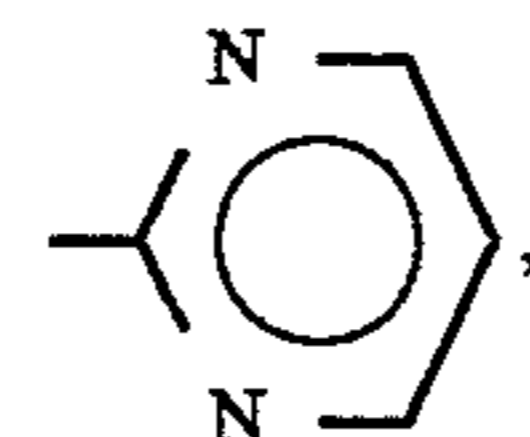
(R)-[4-(5-octyl-1,3-dithian-2-yl)phenyl]2,2-
dimethyl-1,3-dioxolane-4-carboxylate[(I) where $R^1=H_{19}C_8$, $j=1$, $-A^1=$  $k=l=m=zero$, $n=1$, $-A^3=$  $X=O$, $R^2=R^3=CH_3$ and $R^4=H$ Melting point C 129.1°C . $[\alpha]_D^{20}$: +7.1 ($c=2$, $CHCl_3$)

18

EXAMPLE 33

(R)-4-(5-n-octyloxy pyrimidin-2-yl)phenyl 2,2-
pentamethylene-1,3-dioxolane-4-carboxylate[(I) where $R^1=H_{17}C_8$, $j=1$, $-A^1=$  $X=O$, $R^2+R^3=(CH_2)_5$ and $R^4=H$, $k=l=m=zero$, $n=1$, $-A^3=$ Melting point C 111.4° $[\alpha]_D^{20}$: +15.5 ($c=2$, CH_2Cl_2)

EXAMPLE 34

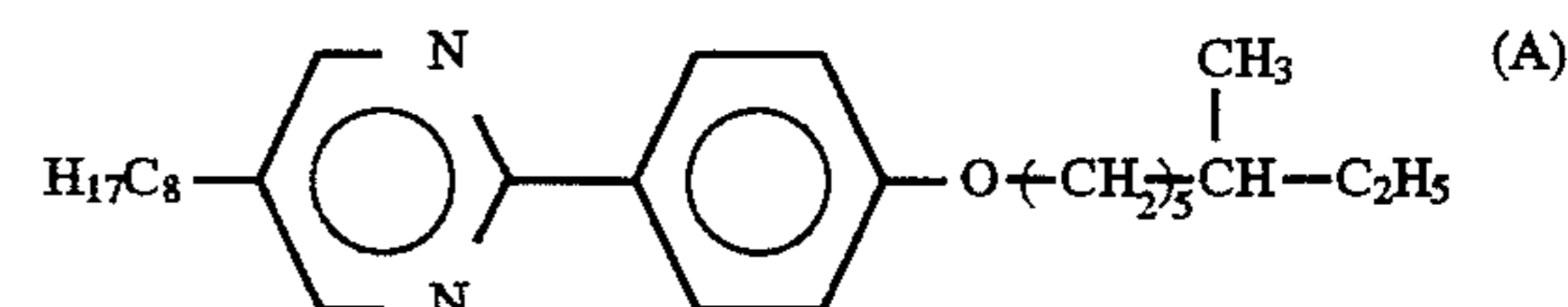
(R)-[2-(4-octyloxyphenyl)pyrimidin-5-yl] 2,2-
pentamethylene-1,3-dioxolane-4-carboxylate[(I) where $R^1=H_{17}C_8O$, $j=1$, $-A^1=$  $k=l=m=zero$, $n=1$, $-A^3=$  $X=O$, $R^2+R^3=(CH_2)_5$ and $R^4=H$ Melting point C 111.6° $[\alpha]_D^{20}$: +16.1 ($c=2$, $CHCl_3$)

Measurement method:

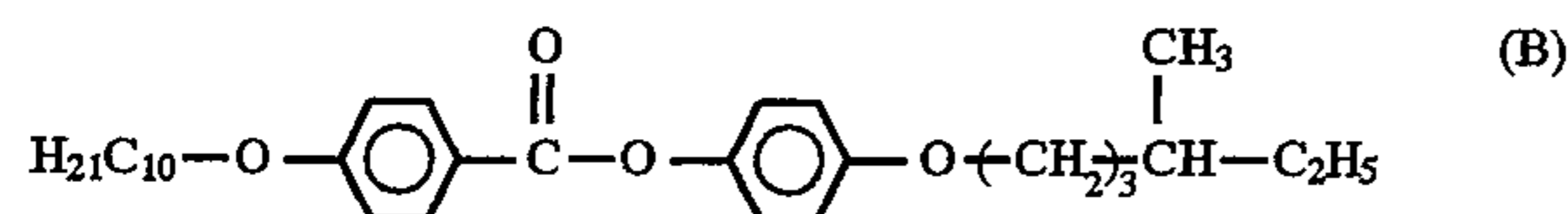
If a small amount of a chiral compound is added to a (non-chiral) solvent, the plane of linear-polarized light is rotated through the (characteristic) angle α ; this angle is specified as follows: $[\alpha]_D^T$ ($c=x$, S), where the symbols have the following meanings: x =concentration of the solution in g/l , S =solvent, $D=589\text{ nm}$ (Na D line), T =temperature of the solution. The angle of rotation is determined in a polarimeter after a light path length of 10 cm.

Use Examples A1 to A18

In order to test the effectiveness of the above-described compounds as ferroelectric dopes in liquid-crystal systems having tilted smectic phases, these compounds are mixed, in concentrations of 10 mol-% in each case, with the racemate of the compound

Phase sequence: C 14.9°C . S_c 49.8°C . S_A 59.2°C . I (5°C)

4-(5-octylpyrimidin-2-yl)-1-(6-methyloct-1-oxy) benzene, or of the compound



Phase sequence: C 17° C. S_G 32.7° C. S_c 70.4° C. S_A 73.3° C. (-3° C.)

4-(4-decyloxyphenyl-1-carbonyloxy)-1-(4-methylhexyloxy)benzene, or of a non-chiral test mixture (C) having the phase sequence: C 13.2° C. S_c 51° C. S_A 61.2° C. N 66.7° C. I, or of a non-chiral test mixture (D) having the phase sequence C 12.5° C. S_c 83° C. S_A 95° C. N 100° C. I, and the values for spontaneous polarization (P_s in nC.cm⁻²), for the switching time τ (in μs) and for the optical tilt angle of the S_c phase θ (in °) of the mixture are determined in each case. The P_s values are measured by the method of H. Diamant et al. (Rev. Sci. Instr., 28, 30, 1957), where a special-purpose measuring cell [Skarp et al. in Ferroelectric Letters Vol. 06, 67 (1986)] is used in which the τ and μ values are also determined. At a cell path length of about 2 μm, a uniform planar orientation of the liquid crystals in the S_c phase is achieved by shearing [SSFLC technique, Clark et al., Appl. Phys. Lett. 36, 899 (1980)]. In order to determine τ and θ, the measuring cell is clamped to the rotating stage of a polarizing microscope between crossed analyzer and polarizer. The optical tilt angle or switching angle 2θ is determined by rotating the measuring cell from maximum to minimum light transmission. The switching time τ is determined with the aid of a photodiode by measuring the time taken for the light signal to increase from a signal level of 10 to 90%. The switching voltage is ±10 V/μm. In addition to the values for P_s, τ, and 2θ, the S_c range of the respective mixture is given, where the values in parentheses indicate the supercoolable lower temperature limit for the S_c region. When compounds (A), (B), (C) and (D) are used as host for accommodation of the dope, all the values for P_s, τ and 2θ relate to a temperature of 25° C. (40° C.).

TABLE 1

(Substance) example	Use example	Host	s _c * region of the mixture in °C.	P _s nC/cm ²	τ μs	2 θ
1	A1	A	31[4] - 54	14	55	52
2	A2	A	37[0] - 53	12.5	35	50
3	A3	A	29,5[4] - 51	11.5	50	49
4	A4	A	13[1] - 51	9	25	41
5	A5	A	18[6] - 52	8	40	41
6	A6	A	[14] - 57	8.3	45	46
8	A7	B	35[35] - 69	9.5	50	59
11	A8	C	15[-8] - 43	9.8	33	40
13	A9	C	11[-5] - 50	12.0	30	46
15	A10	C	12[-7] - 47	8.6	25	40
16	A11	C	15[-6] - 51	8.8	18	41
17	A12	C	17[-6] - 50	7.9	25	37
10	A13	D	10[-6] - 78	26.2	37	64
12	A14	D	11[-10] - 75	23.0	35	64
20	A15	D	[20] - 82	18.1	52	63
22	A16	D		18*	12*	64*
25	A17	D	[5] - 82	20.2	76	61
33	A18	D	[10] - 80	22.3	33	63

*at 60° C.

Use examples A19 and A20

A non-chiral liquid-crystal mixture having the phase sequence I→N→S_A→S_C was admixed with each of the compounds according to the invention, and the twisting

capability (induction of helix) in the nematic phase was investigated. The pitch of the induced helix was determined, as described, for example, by P. Kassubek et al., Mol. Cryst. Liq. Cryst., Vol. 8, pages 305 to 314, 1969, in a wedge cell having an orientation layer by measuring the displacement lines under the polarizing microscope. Table 2 collates the results. As can be seen from the table, both examples exhibit such a large pitch in the N* phase, even at a doping level of 10 mol-%, that pitch compensation by a further optically active dope is not necessary. Example A20 even exhibits helix inversion, which means that the helix changes its direction of rotation and the pitch of the helix becomes infinite.

TABLE 2

(Substance) example	Use example	Proportion of the compound in mol-%	Temperature °C.	Pitch μm	Direction of rotation of the helix*	HTP**)/μm
4	A19	10	60	30	-	-0.33
6	A20	8	65	49.3	-	-0.25
6	A20	8	63.5	∞		
6	A20	8	62.4	46.6	+	+0.27

- (anticlockwise)

+ (clockwise)

**HTP (helical twisting power) = (X · p)⁻¹

X = molar fraction of the dope

p = pitch

Use examples A21 and A22

In orthogonal smectic phases (S_A, S_B and S_E), the compounds of the formula (I) induce the electroclinic effect, the magnitude of which is given by the differential coefficient (dθ/dE). θ is the tilt angle induced by the electrical field E. This parameter is measured in the S_A* phase, but in the same "bookshelf" arrangement and in the same cell as used for the polarization measurements (see Use examples A1 to A18). The tilt angle induced by the electrical field is measured in the polarizing microscope with crossed polarizers by locating the dark positions, reading off the pertinent angle on the rotating stage and subtracting from this the angle measured without an applied field. In order to test the effectiveness of the compounds (I), the electroclinic coefficient of two mixtures was determined. The first (Example A21) was a mixture of (substance) Example 2 (X=0.1) in the racemate A (X=0.9). The second (Example A22) was (substance) Example 4 (X=0.1) with which a non-chiral base mixture of phase sequence I→N→S_A→S_C→C was doped. The values determined in the S_A* phases thus obtained are collated in Table 3. (X=molar fraction).

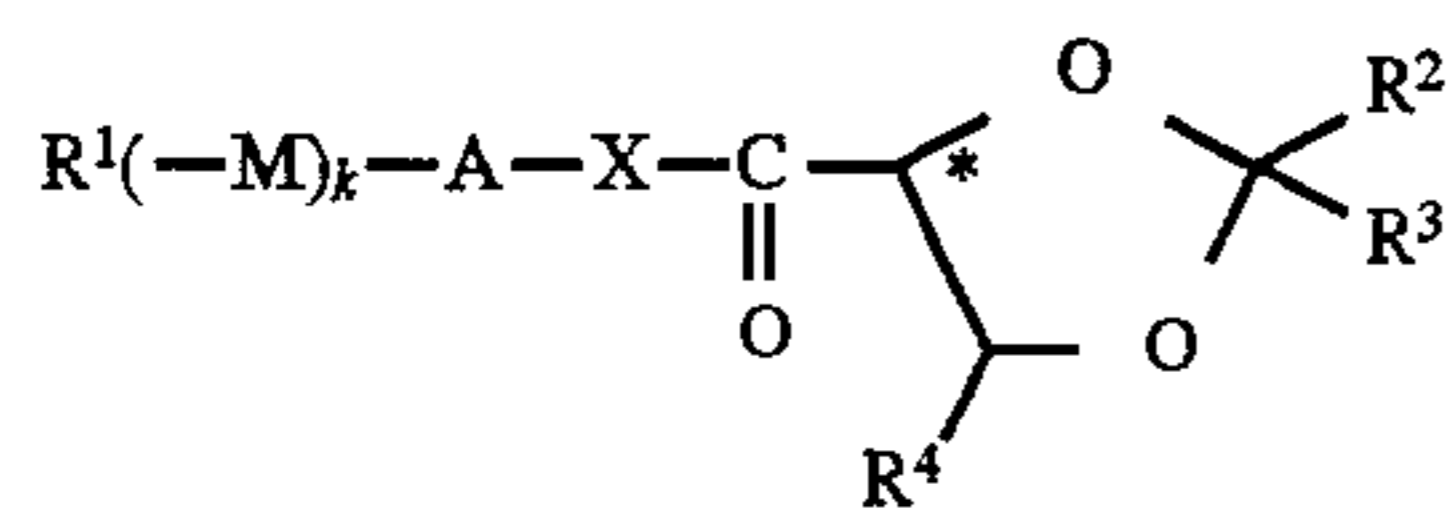
TABLE 3

Use example	Electroclinic coefficients	
	t [°C.]	(dθ/dE) [10 ⁻⁹ rad m/V]
A21	56	2.2
A22	49	5.9
A22	51	3.3
A22	53	2.0

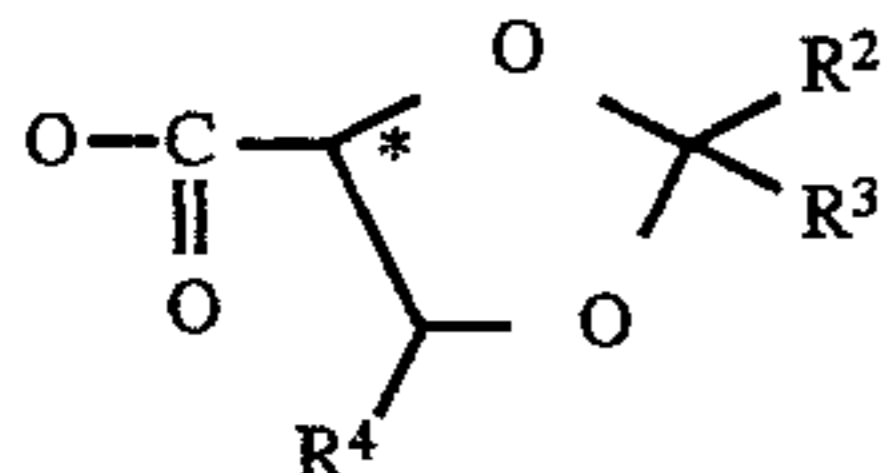
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We claim:

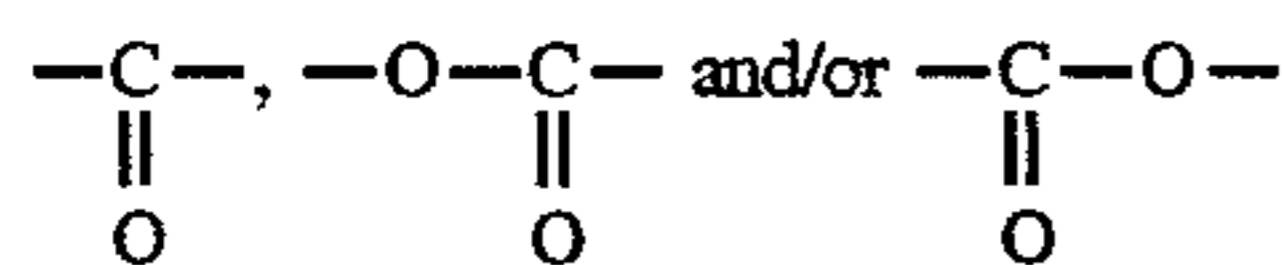
1. An optically active 1,3-dioxolane-4-carboxylate of the formula (I)



in which:

R¹ is

or a straight-chain or branched alkyl radical having 1 to 16 carbon atoms or a straight-chain or branched alkenyl radical having 3 to 16 carbon atoms, it being possible for these radicals to contain asymmetrical carbon atoms and it being possible for one or more nonadjacent —CH₂— groups to be replaced by —O—, —S—,

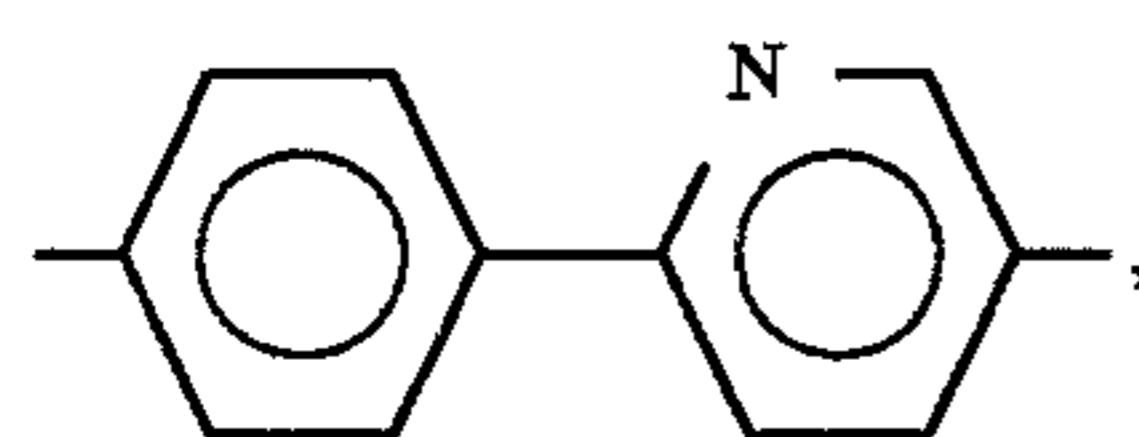
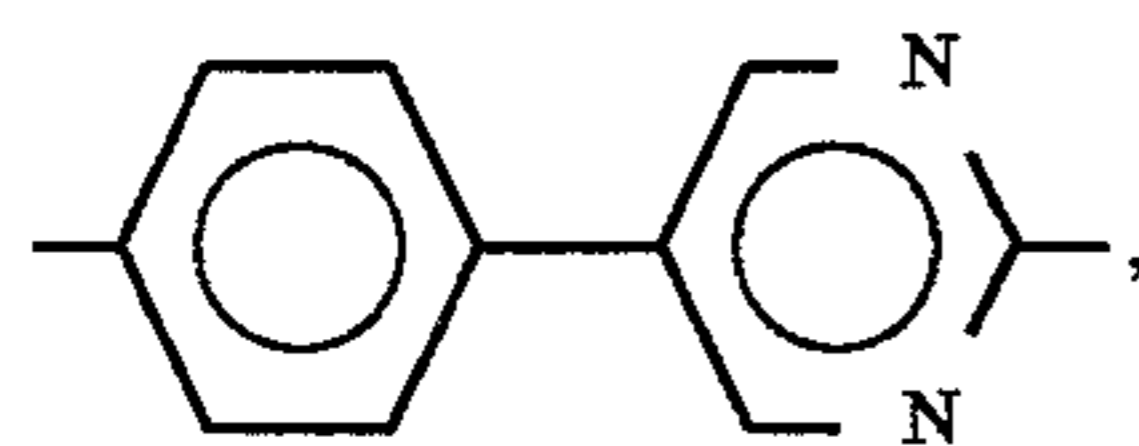
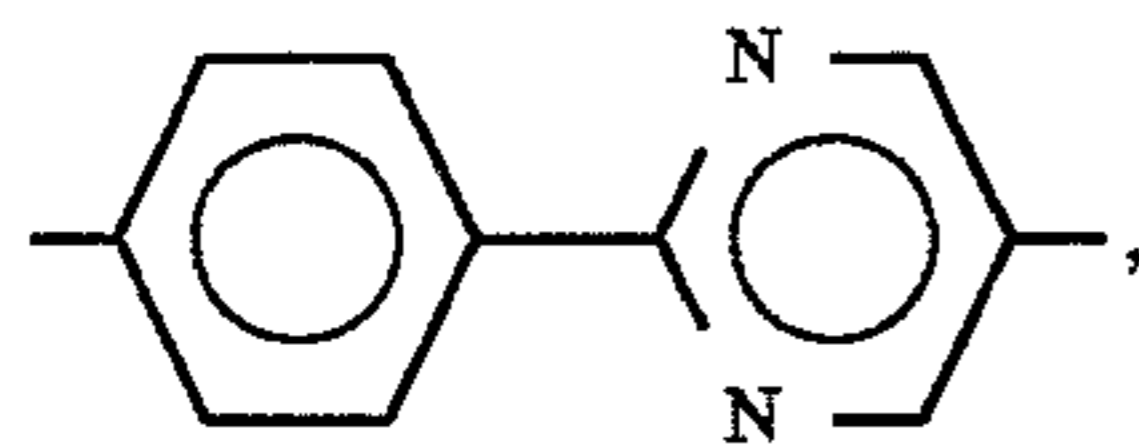
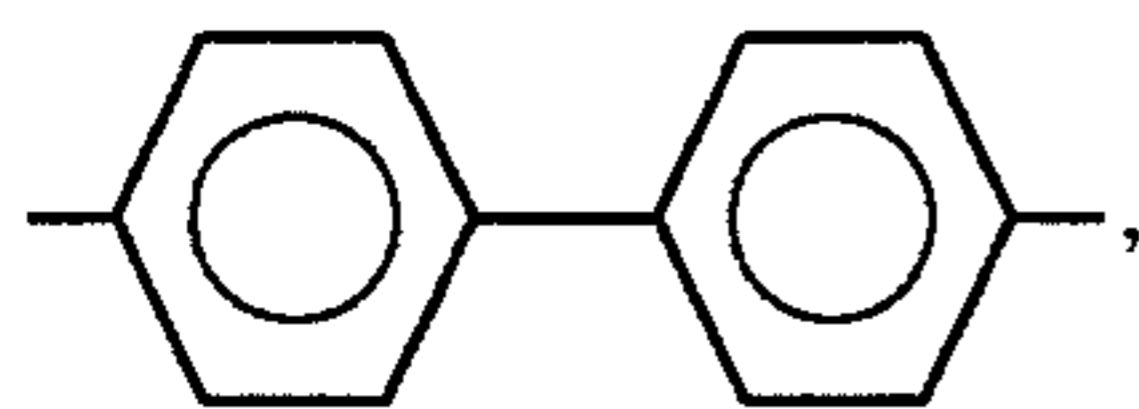


and for one or more H to be replaced by F, Cl, Br or CN, R² and R³ are each H or an alkyl radical having 1 to 10 carbon atoms, it being possible for one or more H of the alkyl radicals to be replaced by F; or R² and R³, together with the C(2) atom of the dioxolane ring, form a cyclopentane, cyclohexane or cycloheptane ring,

R⁴ is H or an alkyl radical having 1 to 10 carbon atoms or an alkenyl radical having 2 to 10 carbon atoms,

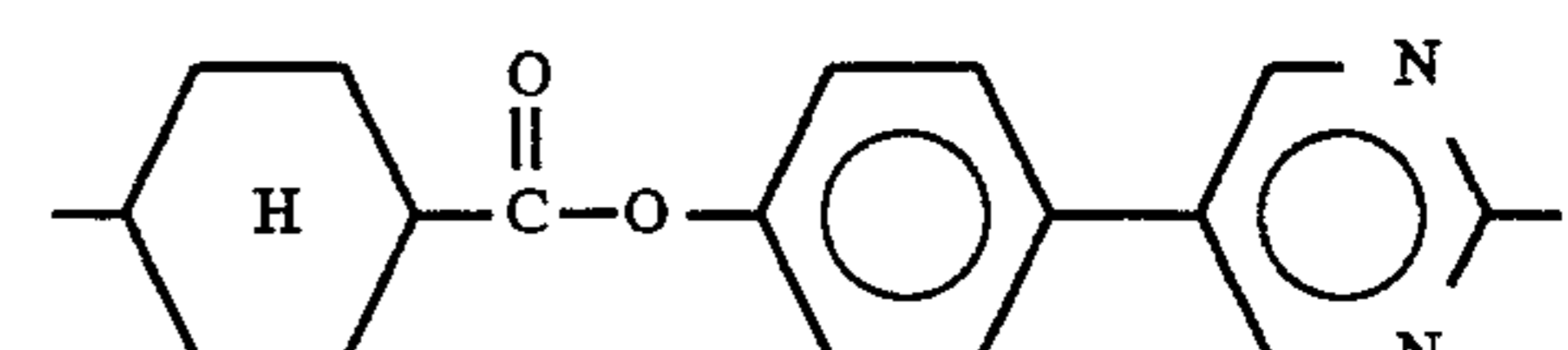
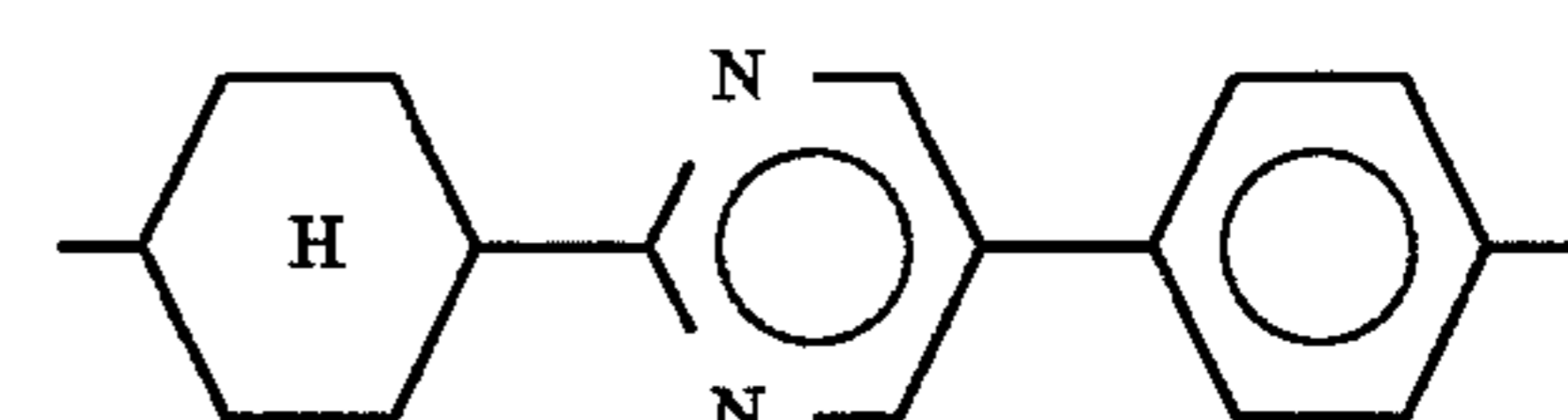
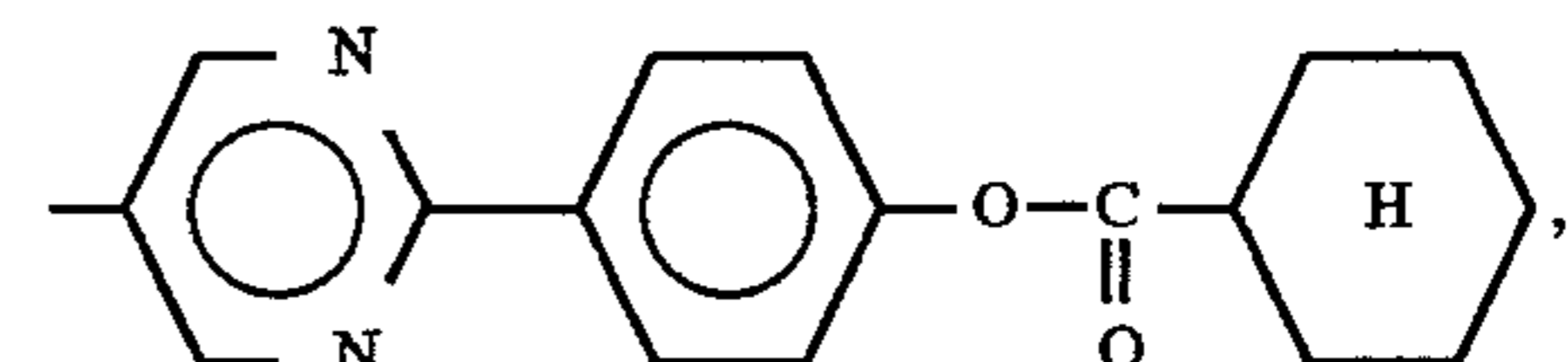
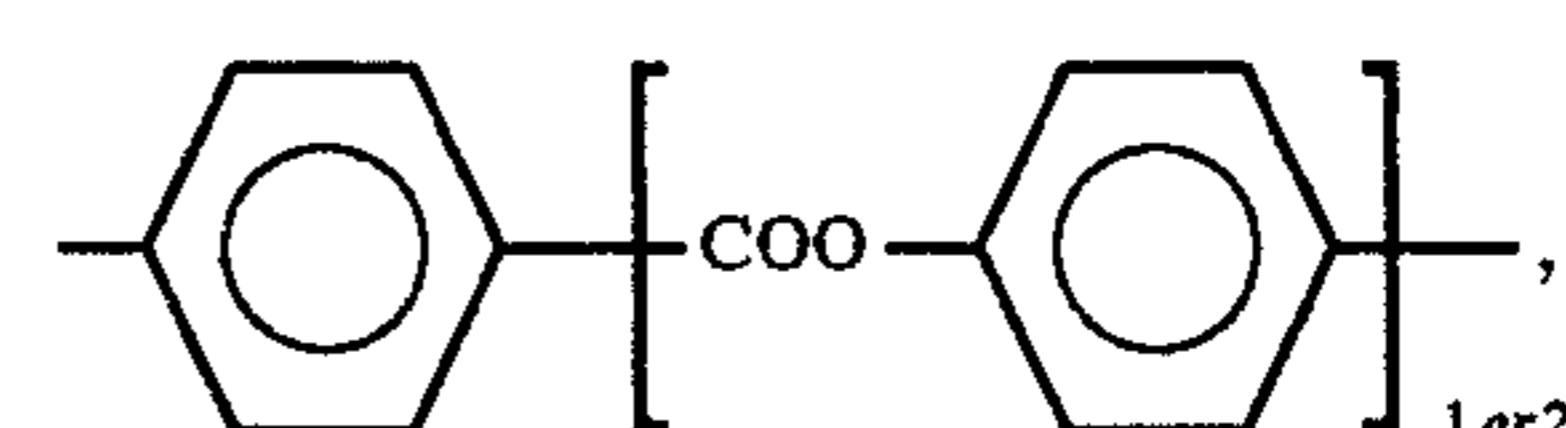
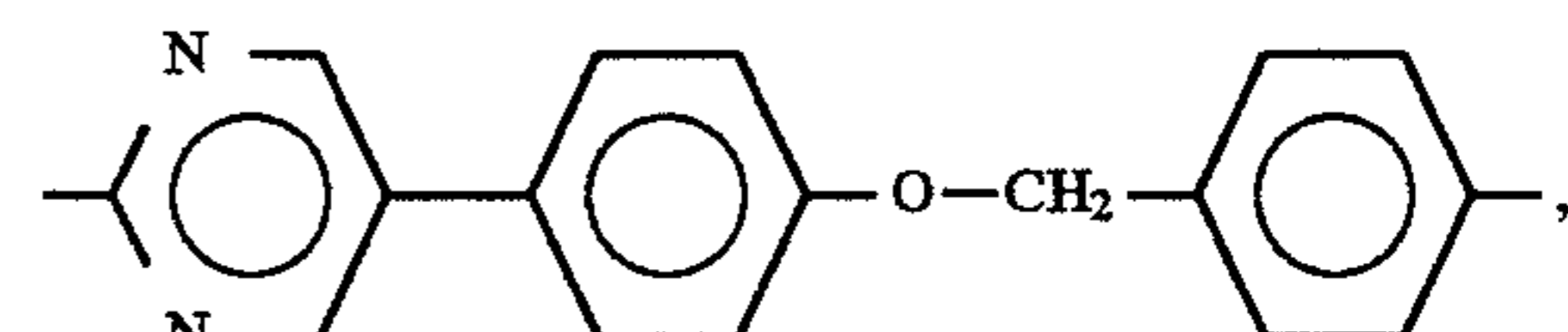
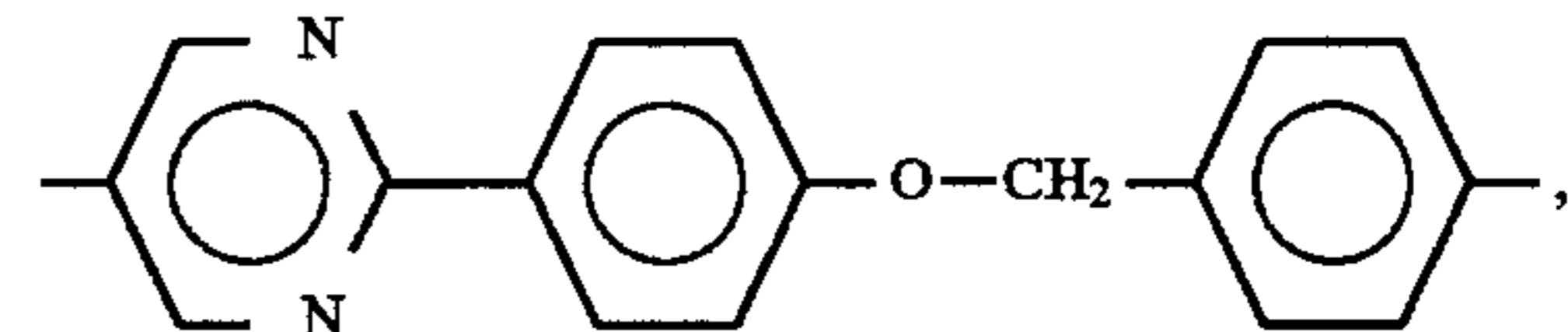
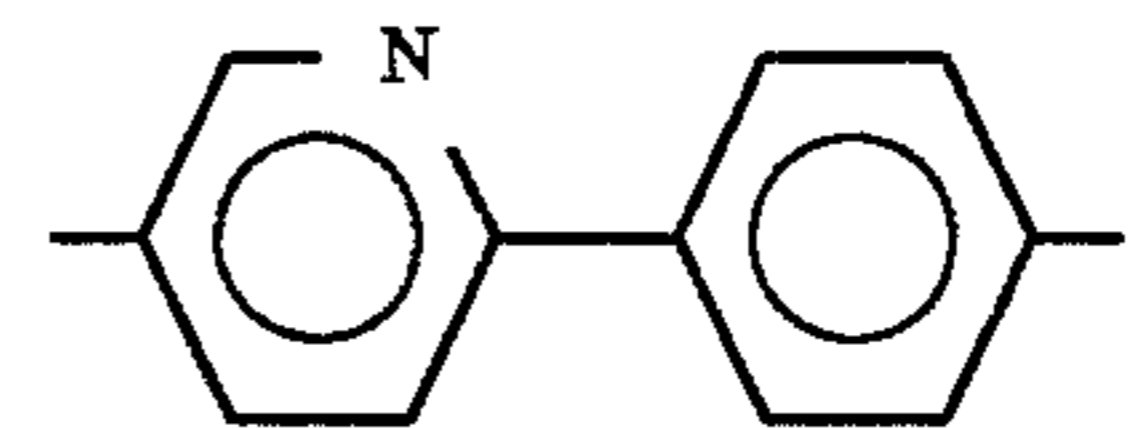
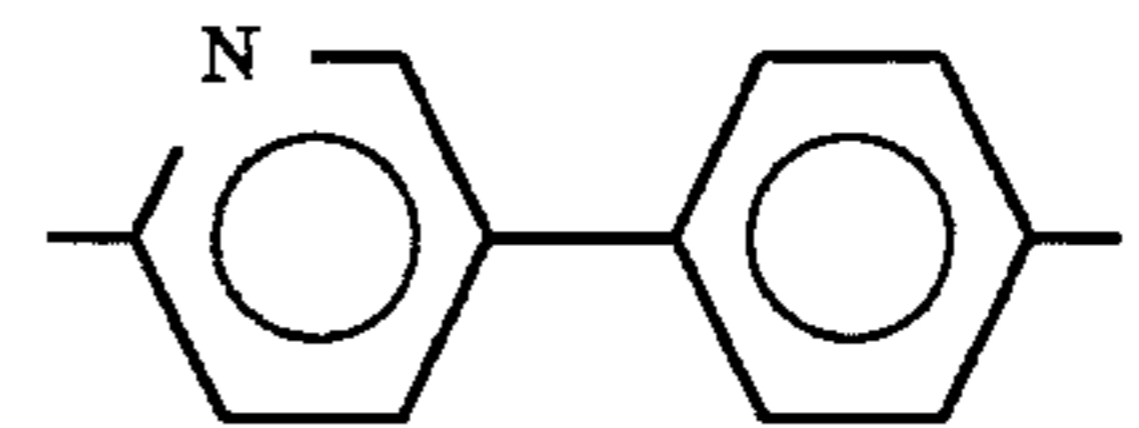
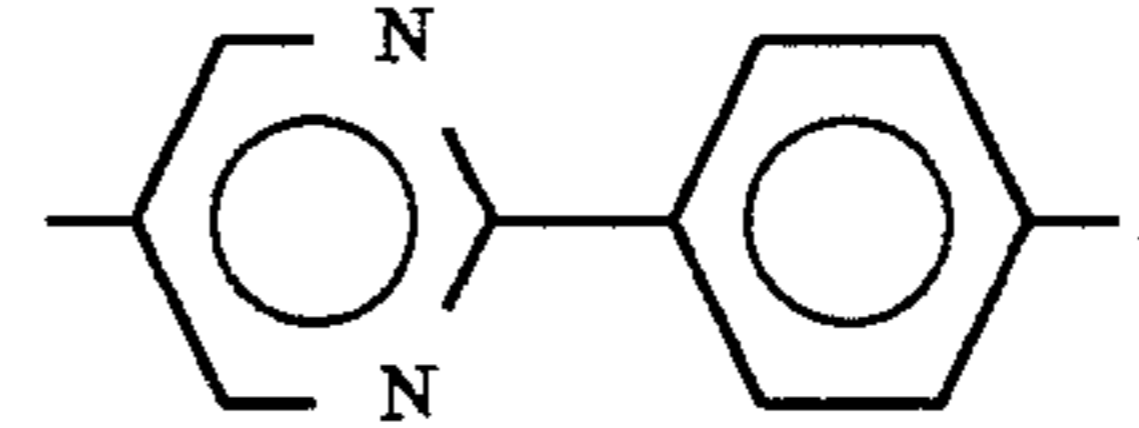
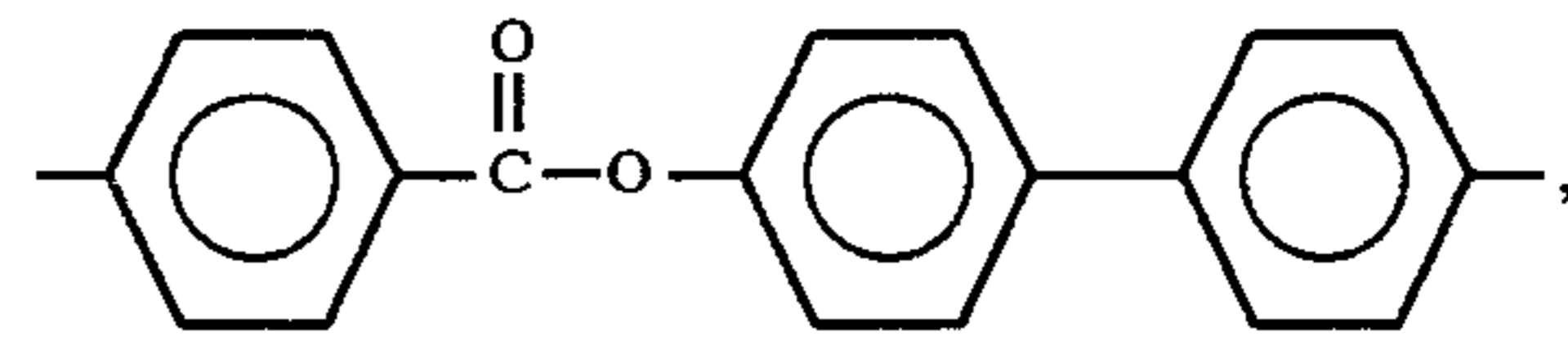
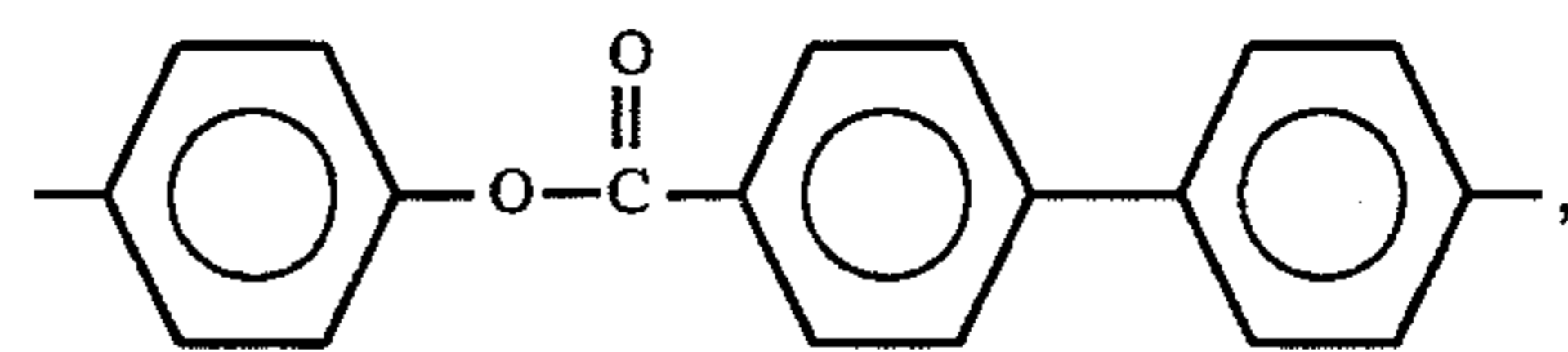
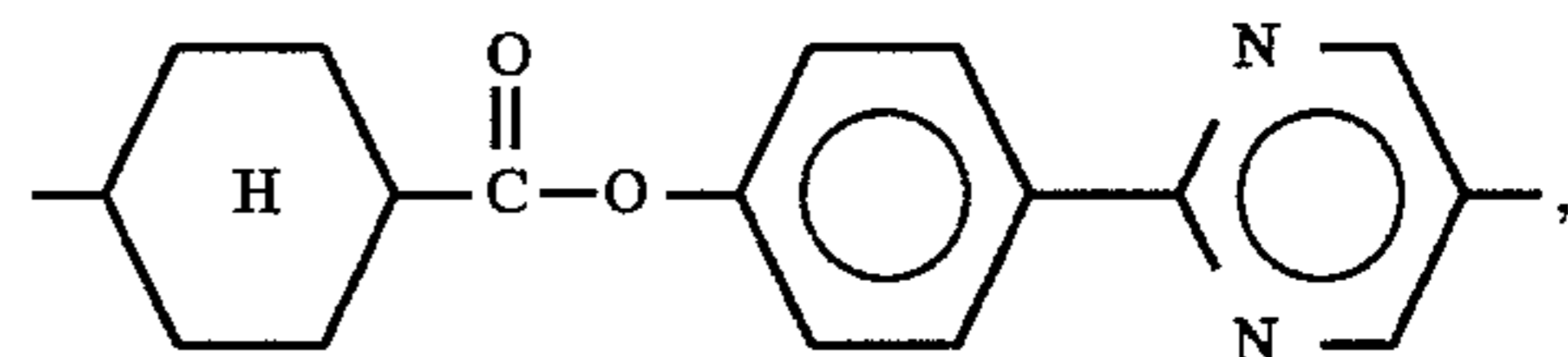
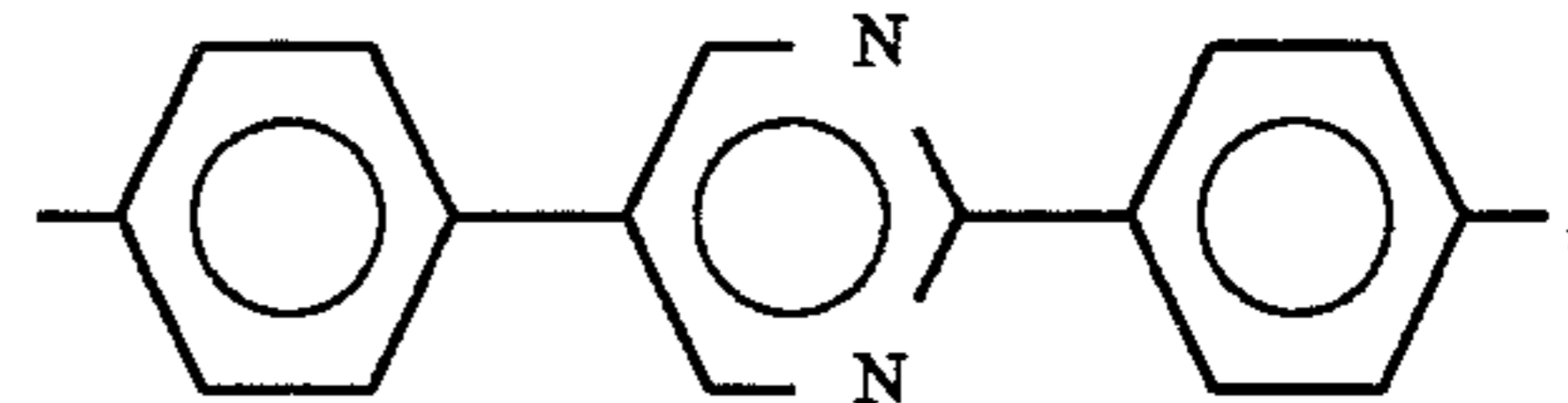
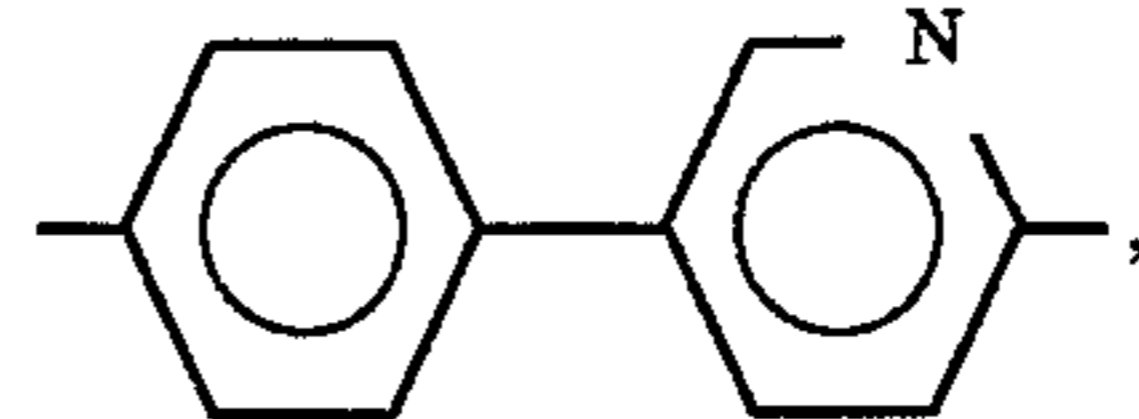
k is zero or 1, with the following proviso that k is zero, if R¹ is a dioxolane group or an alkyl group with a replaced —CH₂— group,

—A— is:

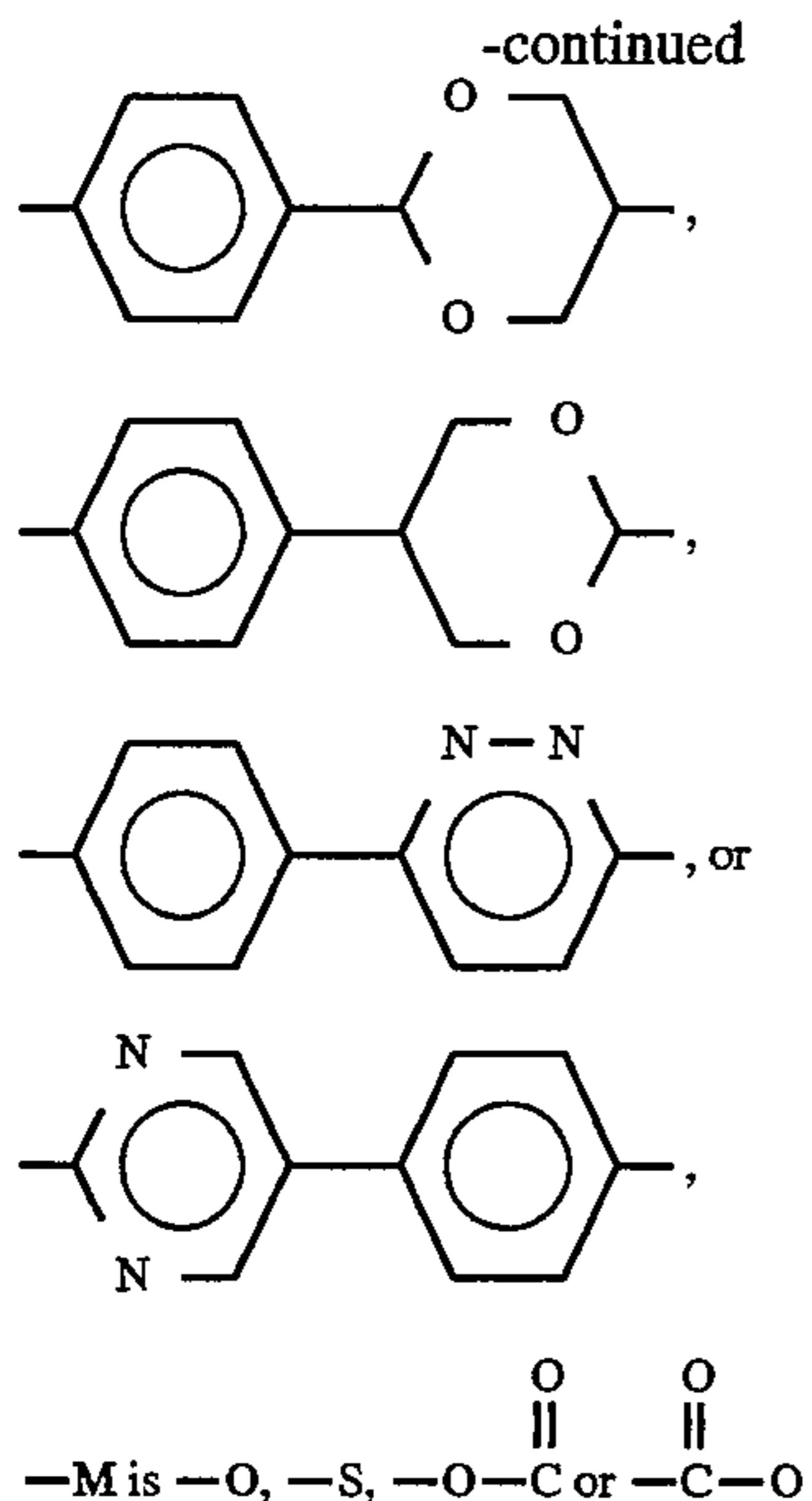


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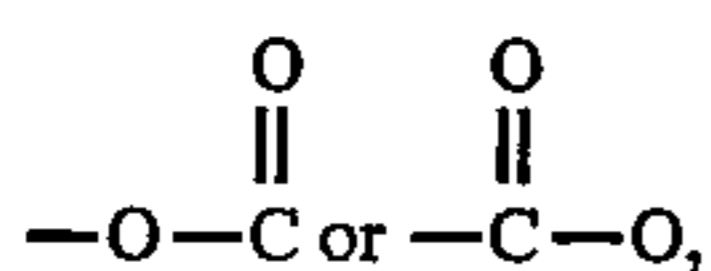
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and

-X is $-\text{O}-$ or $-\text{S}-$.

2. An optically active 1,3-dioxolane-4-carboxylate of the formula (I) of claim 1, in which R^1 is a straight-chain or branched alkyl or alkenyl radical which has 6 to 12 carbon atoms and which may contain asymmetrical carbon atoms,

-M is $-\text{O}-$, $-\text{S}-$,

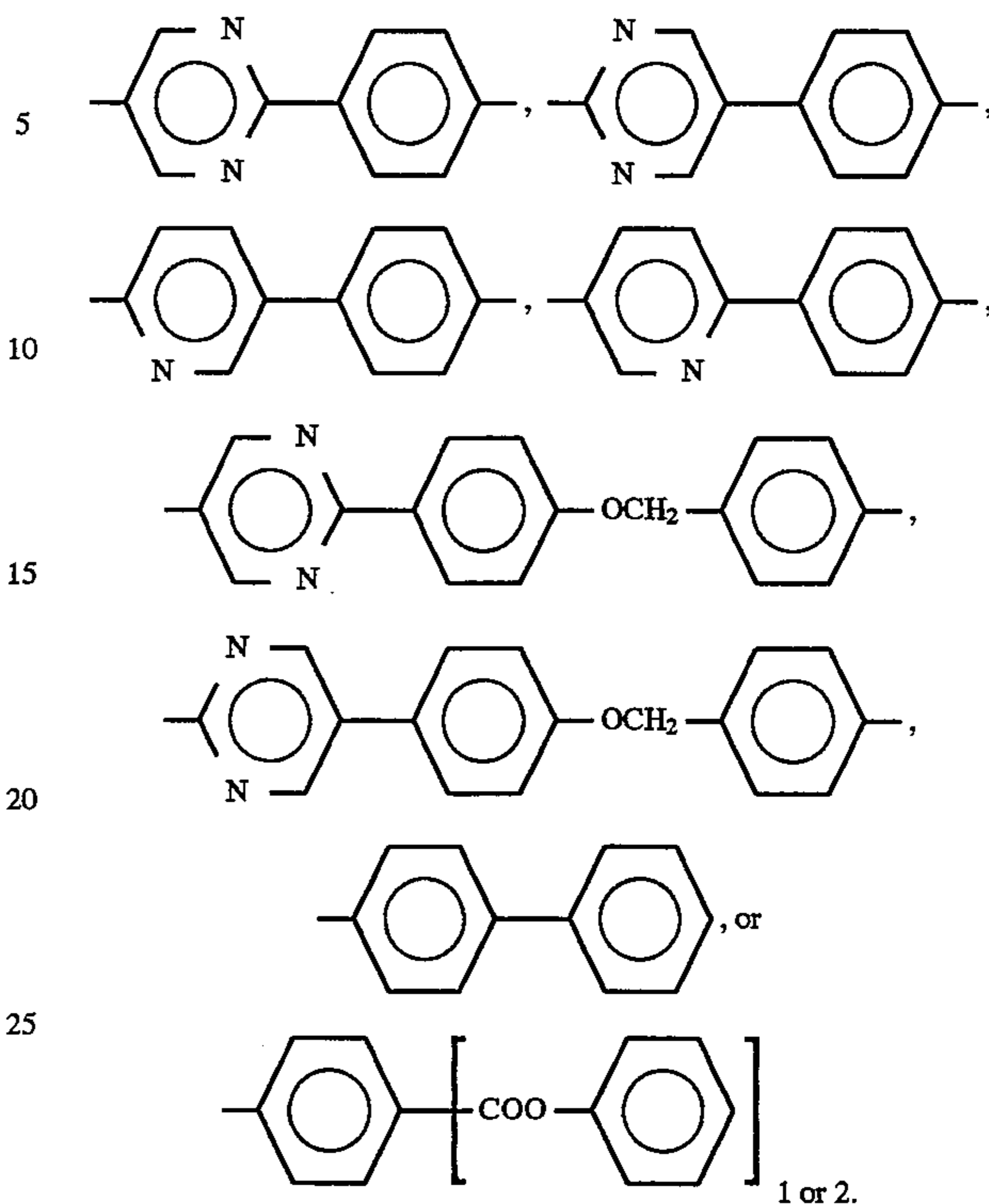
R^2 and R^3 are CH_3 or R^2 and R^3 together with the C(2) atom of the dioxolane ring form $-(\text{CH}_2)_5-$,

 R^4 is H,-X is $-\text{O}-$ or $-\text{S}-$,

k is zero or 1, and

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-A- is:



3. A liquid-crystal mixture containing at least one optically active compound of the formula (I) of claim 1 and a component selected from compounds having nematic, cholesteric and/or smectic phases.

4. A liquid-crystal mixture containing at least one optically active compound of the formula (I) of claim 2 and a component selected from compounds having nematic, cholesteric and/or smectic phases.

5. An electrooptical switching or display element containing a liquid-crystal mixture as claimed in claim 3.

6. An electrooptical switching or display element containing a liquid-crystal mixture as claimed in claim 4.

* * * * *